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ULTRAFINE POLYBENZIMIDAZOLE (PBI) FIBERS

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E. C. Chenevey

CELANESE RESEARCH COMPANY
a division of
CELANESE CORPORATION

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-20040
Dean W. Sheibley, Project Manager

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Final Report

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Solar and Electrochemistry Division

FOREWARD

The research described herein was conducted by the Celanese Research Company, a division of Celanese Corporation, under the direction of Dr. Edward C. Chenevey, Principal Investigator. Dr. Joseph R. Leal served as Project Coordinator and Contract Administrator. The work was managed by Dean W. Sheibley, NASA Project Manager, Solar and Electrochemistry Division, NASA Lewis Research Center.

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ABSTRACT

Mats were made from ultrafine polybenzimidazole (PBI) fibers to provide an alternate to the use of asbestos as separators in fuel cells and alkaline batteries.

To minimize distortion during mat drying, a process to provide a dry fibrid was developed. Two fibrid types were developed: one coarse, making mats for battery separators; the other fine, making low permeability matrices for fuel cells. Eventually, it was demonstrated that suitable mat fabrication techniques yielded fuel cell separators from the coarser alkaline battery fibrids.

The stability of PBI mats to 45% KOH at 123°C can be increased by heat treatment at high temperatures. Weight loss data to 1000 hours exposure show the alkali resistance of the mats to be superior to that of asbestos.

SUMMARY

Fibrid technology applied to PBI produced a film-like fibrid which was readily fabricated into light-weight porous handsheets. Shrinkage and wrinkling during drying occurred, however, with larger sheets. Careful washing to remove residual solvent followed by "preshrinking" fibrids in toluene and azeotropically distilling off the water, gave a dry fibrid which could be rewetted and fabricated into a mat or paper with less than 5% shrinkage.

Two types of PBI fibrids were prepared, one for alkaline battery separators, the other, for fuel cell matrices. Both the alkaline battery and fuel cell fibrids were similar except that one was more coarse than the other. Recently, it was demonstrated that mats for both alkaline batteries and fuel cells can be prepared from the coarser fibrids, originally developed for alkaline batteries, by appropriate calendering techniques.

The Schweitzer Division of Kimberly-Clark Corporation made a continuous length of 30 cm (12 in.) web on conventional paper-making equipment. However, inadequate removal of solvent led to subsequent fusion on the dryer cans and the "paper" so produced was unsatisfactory. Because of a limited supply of fibrids, the run was not repeated. However, a quantity of 30 x 60 cm (12 x 24 in.) handsheets were made using technology that is in general use by those engaged in paper manufacturing.

After various PBI fibrid samples had been evaluated, it was noted that some samples had better resistance to hot alkali than did others. After verification of these observations, it was found that heat treatment of a mat in an air oven at 375°C for one hour, or until the mat is no longer soluble in dimethylacetamide, will substantially improve the resistance of the mat to hot concentrated alkali (45% KOH at 123°C). With a 2% weight loss after 1000 hours, the heat treated mats have a greater resistance to hot alkaline solutions than do separators and matrices made from asbestos.

RECOMMENDATIONS

Sufficient samples of both fibrids and mats have been delivered to NASA to allow their evaluation in operable fuel cells or alkaline batteries. Mats should be heated in an air oven at 375°C for an hour or until they are oxidized sufficiently so that they no longer dissolve in dimethylacetamide. The resulting mats shoud possess outstanding resistance to hot concentrated alkali.

Scale-up would require the use of a continuous paper machine. In this case, shrinkage upon drying is an advantage since it would provide a stronger sheet. The accompanying wrinkling would be taken care of by tension in the machine direction. For this purpose, a water washed but not dried PBI fibrid would probably be preferred. Some amount of PBI textile fiber could also be added to improve strength. Such development should be undertaken jointly with a papermaker in order to integrate and optimize fibrid preparation and mat making.

INTRODUCTION

The polybenzimidazole (PBI) polymer, poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, is known to possess outstanding thermal, physical and chemical stability over nearly the entire pH range (1-7). At Celanese, several thousand pounds of polymer have been produced over the past fifteen years (8,9). Much of this polymer was converted into textile fibers and yarns for test and evaluation in Air Force and NASA applications requiring non-flammable woven, knitted or braided flexible structures (e.g. flight clothing and lanyards) (10-13).

The polymer has also been converted into hollow fibers and flat sheet for studies at Celanese of its utility as a reverse osmosis membrane (14,15). In this application, PBI has exhibited excellent rejection properties of aqueous salt, urea and detergent mixtures at pasteurization temperatures (16). More recently, it was investigated under EPA support as a reverse osmosis membrane to treat chromic acid electroplating solutions (17). Despite the low pH and the strongly oxidizing medium, the PBI membranes were shown to be unaffected by either the acidity or the oxidative strength of the chromic acid.

In addition to the work performed at Celanese, others have examined PBI polymers, fibers and films for a number of different applications (18-23). Among these have been tests to determine its utility in advanced fuel cell and battery systems. In at least one instance, a mat of PBI fibers lost only about 1% of its weight when immersed for 5000 hours at 250°F in concentrated KOH solution saturated with oxygen (24). In addition, the PBI fibers exhibited a satisfactory degree of hydrophilicity. On the other hand, the coarseness of the conventional PBI textile fibers being tested precluded the fabrication of a separator with bubble pressures comparable to those obtained with asbestos fibers.

The purpose of this contract was to determine whether PBI could be converted into ultrafine fibers suitable for the formation of mats which could be used as an alternate for asbestos in advanced fuel cells and batteries. Several approaches for the preparation of ultrafine fibers from PBI were available. However, the most economical scheme was found to be the one that revolved around the so-called fibrid process. For that reason, the fibrid approach was chosen for the initial effort and remained the method of choice throughout.

Fibrids, which are short "fiber-like" materials with a somewhat irregular shape, are produced by coagulation of a polymer solution in a shear field which attenuates the polymer as it is being precipitated. The result is the formation of a hairy "fiber-like" material. Fibrids are ideal for paper or mat making since their very irregularity leads to a strong degree of mechanical interlocking which can provide strength without additional bonding steps.

This report covers the preparation of PBI fibrids and the preparation and characterization of both high and low permeability mats from them. Subsequent heat treatment of these mats in air has been shown to increase their resistance to attack by hot concentrated alkali.

OBJECTIVES AND STATEMENT OF WORK

The purpose of this effort is to produce fibers from polybenzimidazole (PBI) polymer, poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, which have a diameter range from 0.1 to 1 micron and a length to diameter ratio of 100 to 1000, generally regarded as suitable for matrix fabrication. The matrix materials made from these fibers should be a viable substitute for asbestos in fuel cells and nylon in alkaline batteries.

Task I - Production of Ultrafine Fibers from PBI

Established conventional extrusion technology and "fibrid" formation techniques shall be applied to PBI polymer for the purpose of achieving ultrafine filaments in the diameter range of 0.1 - 1 micron. The feasibility of making the ultrafine PBI fibers shall be determined by one of the established techniques used for:

1. Fibrids preparation
2. Conventional spinning processes
3. Spray spinning

Mat preparation from the resulting ultrafine fibers shall be demonstrated.

Task II - Establish Sequence of PBI Fibrid Treatments for Finished Product

A sequence of treatments of PBI fibrids shall be established so that the finished PBI fibrid product possesses characteristics of being rewettable and redispersible for application to both fuel cells and alkaline batteries. The fibrid products produced in Tasks III and IV (below) shall exhibit only minimal or no shrinkage and no cracking in dry mat form. It is desirable that the finished form of the fibrid for both applications be dry rather than wet.

Task III - Establish Process Methods for Producing Fibrids for Fuel Cell Application

An investigation of the methods necessary for producing fibrids which will produce a matrix suitable for fuel cell use shall be made. This matrix shall possess flexibility and integrity and exhibit a bubble pressure of greater than 20 psi but less than 60 psi in 45% KOH and after 30 days of exposure

to 45% KOH solution at 90°C, rinsing with water, and exposure again to 45% KOH at 90°C. The matrix shall be 0.010 inch thick. Integrity is defined as possessing sufficient strength such that a piece 1 foot long supported on one edge will support itself, either wet or dry. Acceptable flexibility will be demonstrated by bending over a diameter of 8 inches in dry form. Such bending shall not change the bubble pressure of the matrix.

The Contractor shall provide NASA with enough fibrids for making about 1 square yard of matrix material. This may be supplied in several batches as work progresses. In addition, the Contractor shall provide NASA with four (4), 6-inch x 6-inch mats made from the fibrids. These mats shall be within the range of specifications noted above.

Task IV - Fibrids for Alkaline Battery Separator-Absorber Use

Using sample materials provided by NASA under Task I, namely, the 10-mil fuel cell grade asbestos, and non-woven nylon (Pellon No. 2506) as examples of extremes of sample properties, the Contractor shall investigate the methods necessary for producing PBI substrate for battery separator-absorber use. Substrate thickness shall be in the range of 4 to 7 mils with the 5-mil thickness most desirable. Area resistivity should be 0.2 ohm-cm2 or less in 35% KOH solution. The substrate must be flexible and uniform, capable of being bent over a 1/4 inch mandrel without cracking in dry form. The Contractor shall fabricate and provide to NASA, eight (8) pieces of PBI substrate made from finished fibrids (8-inch x 8-inch) for cell test evaluation.

Task V - Increase Stability of PBI Fibrids

The Contractor shall determine the necessary heat treatment to thermally crosslink PBI fibrids to improve weight loss resistance in hot potassium hydroxide solution. The method of thermal crosslinking developed should be compatible with the existing sequence of fibrid processing techniques which provide a dimensionally stable mat. Requirements specified in Tasks II, III, and IV should be met by the crosslinked fibrids. The weight loss goal shall be less than 1.5% after being immersed in 45% KOH for 5000 hours at 250°F.

When the weight loss is minimized, the Contractor shall then thermally crosslink ~ 20 pounds of fibrids to be supplied by NASA.

EXPERIMENTAL

A. PBI Polymer

Polybenzimidazole (PBI) or more properly, poly-2,2'-(m-phenlyene)-5,5'-bibenzimidazole, is a thermally resistant polymer prepared by the melt condensation of 3,3'4,4'-tetraaminobiphenyl (TAB) with diphenylisophthalate (DPIP) in a two step process. During the first stage, the monomers melt, react, and form a low molecular weight polymeric foam. This foam is crushed and reheated during the second stage to produce the final high molecular weight PBI polymer. Typical polymer is a tan to brown solid with an inherent viscosity (IV) of 0.7 to 0.8 deciliters/gram (dl/g) in sulfuric acid (0.4 g/100ml of 97% sulfuric acid). Besides acid, PBI is soluble in highly polar solvents such as dimethlformamide, dimethylacetamide, and dimethylsulfoxide. Dimethylacetamide (DMAc) containing 2% lithium chloride (LiCl) is the preferred solvent which has been used at Celanese to spin textile fibers from PBI.

B. Dope

To prepare fibrids, a solution of polymer (dope) is required. All dope used to prepare fibrids under this contract was made using DMAc containing 2% LiCl as a stabilizer.

Three sources of dope were used. Initial trials used PBI dope obtained from previously prepared and filtered fiber spinning dopes diluted with DMAc to lower the solids level from 24 to 11%. Target viscosity was 4-5 poise (Brookfield RVT, spindle No. 2 at 10 rpm, 20°C). Samples were diluted to a specific viscosity, not to a solids level. The use of 100% DMAc for dilution resulted in a lowering of the LiCl stabilizer level of the dope, but it was felt that no stabilizer was necessary at the low solids level used.

After the preexisting dope supply was exhausted, a batch of dope was prepared by redissolving previously spun textile yarn, filtering, and then diluting to 5 poise. Once Celanese resumed production of PBI polymer, a new dope batch at 24% solids was made fom polymer P(2039-40-38)A, a typical PBI polymer with an IV of 0.75 dl/g. Standard PBI solutioning conditions were used, heating the polymer with DMAc

containing 2% LiCl at 220°C for two hours. After cooling to about 100°C, filtration through a depth type cellulose paper filter media was done to remove the normal granular insolubles (~1%) and any gel-like particles. After dilution to target viscosity, (4-5 poise) all dopes were crudely filtered through a layer of polypropylene felt to remove any trash picked up during transfer and handling.

C. Apparatus

Fibrids are produced by coagulating a polymer solution or dope in a shear field thereby attenuating the dope during the coagulation process to prepare "fiber-like" particles or fibrids. Many types of devices capable of mixing a polymer solution with a coagulant have been described in the literature. For this project, a commercial internal mix spray nozzle was used to prepare the fibrids. The basic apparatus needed to prepare fibrids is very simple, a polymer dope feed assembly, a source of coagulant, and the mixing device.

PBI dope, as described previously, was prepared and filtered off line. As needed, dope was manually transferred to a reservoir of approximately one gallon capacity which was fed by gravity to a textile fiber dry spinning type gear metering pump (Zenith 5B, Zenith Products Co., W. Newton, Mass. 02165). The pump was connected to a pressure gauge and fed dope to the fluid side (center) of the spray nozzle.

For coagulant, deionized water was used. Water pressure was boosted with a high pressure piston pump (Teel 1P741, W. W. Grainger, Inc., Newark, N. J. 07102). Pump output pressure was controlled by use of an adjustable relief valve which bypassed fluid back to the inlet. In addition to a thermometer and pressure gauge, an air containing ballast tank was connected in line to reduce the pressure surges which the reciprocating piston pump produced. This high pressure water was fed to the air side (outer) of the spray nozzle.

The nozzle assembly employed was a Spraying Systems Co. (Wheaton, Ill. 60187) 1/4 J internal mix round spray pneumatic atomizing nozzle, system No. 12A, consisting of fluid nozzle 2050 with air cap 73160. In the laboratory, the fibrids were collected in tared 1-5 gallon containers while in the pilot plant the fibrids were directly sprayed into a tank with gravity flow to a centrifuge.

After-processing consisted of boiling the fibrids with water to remove residual solvent and then dewatering the fibrids by azeotropically distilling water from a toluene suspension of fibrids. In the laboratory, common glassware was used, the samples being boiled in a beaker and filtered via gravity with a piece of cotton muslin. Azeotroping was done in a 5 liter, 3-neck flask equipped with a stirrer, azeotrope trap, condenser, and nitrogen bleed. Again, filtration was by gravity through a piece of muslin followed by air drying in a hood and finally an oven dry to drive off the residual toluene.

In the pilot plant, separations were done with a basket centrifuge and both the washing and azeotroping were done in a 400 gallon stainless steel kettle equipped with a turbine agitator, condenser, and azeotrope splitter. The slurry would flow by gravity to the centrifuge. Fibrids were place on large trays covered with cheesecloth and allowed to dry, first in air and subsequently in an oven.

D. Fibrid Formation

A filtered PBI dope in DMAc was prepared with a 4-5 poise viscosity at 20°C. The Zenith metering pump had a capacity of 2.92 cm^3/revolution and was normally set with a speed of 5 revolutions in 18 seconds or 48.7 cm^3/min.. These PBI dopes have a density of 0.996 g/cm^3, thus giving a normal nominal feed rate of 48.5 g/min.. With approximately 10.5% solids, the solid feed rate was 5 g/min. or 300 g/hr.

Depending on the desired fibrid properties, deionized water pressures of 125-300 pounds/sq. inch (psi) were used. Flow rates were proportional to pressure and were on the order of 3 liters/minute (l/min.) at 300 psi thus yielding a 0.16% slurry of PBI fibrid in water containing 1.4% DMAc.

E. Fibrid Afterprocessing

Four boiled deionized water washes were used to remove DMAc from the fibers. The concentrations were not critical, the only requirement being that the system be stirrable and capable of being discharged from the vessel. About 1135 l (300 gal.) of water were used to wash 120-150 lb. of wet fibrids. In the case of the fine fuel cell fibrids, the wet centrifuged fibrids contained 6.9% solids. Coarser fibrids for battery separators had a solids level of 16.4%. A fairly dry cake was desired since fibrids which were too wet tended to stick together and form beads during the azeotropic drying.

For azeotropic drying, the damp fibrids were charged into the reactor with toluene at a level of 0.3-1.1 kg (0.7-2.5 lb.) fibrids per 3.8 l (1 gal.) of toluene and were azeotroped until no further water came off. After centrifuging, a 19.4% solids toluene-wet fibrid was obtained.

Due to the large amount of toluene to be evaporated, the fibrids were allowed to air dry at least overnight prior to a vacuum oven drying at 80°C.

F. Ultrafine Fibrids

A very fine PBI fibrid was made by using a 70/30 mixture of DMAc/H_2O as the coagulant rather than water alone as was the usual case. The DMAc-water mix was made up in a 55 gallon drum and was set-up for a gravity feed to the coagulant pump. A tee connection and valves were provided to enable switching from water to the DMAc-water mixture. The same nozzle and dope feed settings were used as for the normal fibrids. To conserve the blended solvent, fibrid formation was started using water and was then shifted to the coagulant blend after stable operation had been achieved. Coagulant pressures of 180-225 psi were used. The product was collected in a tank and transferred to stainless steel drums for storage. This slurry contains 70.3% DMAc, 0.15% PBI, and the remainder, water. It was used as such for addition to the paper making slurry.

G. Preparation of Mats

Mats were prepared by filtration of a fibrid slurry in water. A dry fibrid sample, calculated to provide the desired mat weight of 30-120 grams/meter (g/m), was allowed to remain in deionized water for a minimum of an hour to rewet the fibrids. Any lumps were broken up by hand. This slurry was then dispersed using a Waring blender and the slurry poured into a hand sheet box or a coarse fritted glass funnel where the sheet was made by filtration. Some mats were made directly on the fritted glass surface of the funnel, however, most were made on a sheet of Whatman No. 1 filter paper. Either a fine screen or filter paper was used as the formation surface in the paper making hand sheet box.

After the sheet was sucked down on the surface, it was removed and overlaid with a sheet of filter paper. The sheet was then lightly rolled by hand to compact it. The wet filter paper was stripped off and replaced with dry paper. Some samples were further compacted or densified by being passed

through a set of calender rolls. The PBI mat was protected during this operation with filter paper on each side. As it became wet from water squeezed out during calendering, the paper was replaced. Multiple passes were used in 90° different directions in order to maximize uniformity.

Calendered or non-calendered samples were dried by placing dry filter paper on each side, interleaving them with sheets of 19 millimeters (mm) (3/4 in.) plywood and placing weights on top to press them flat. The resulting stack was allowed to air dry for several days, changing the damp filter paper every day.

H. Mat Characterization

1. Weight and Density

Basic mat characterization consisted of the determination of true basis weight in grams per square meter (g/m^2) by simply weighing the mat and measuring it. Thickness measurement was much more difficult since the mats are readily compressible. Initially a TSI Electronic Micrometer was used. Later, a Mitutoyo dial indicator No. 2109 reading to 0.001 mm was used with a 1 cm diameter measuring surface. Since all samples have thickness variations on the order of ±15%, this accuracy is unnecessary. Using the average thickness, a mat density could be calculated. This fell in the region of 0.15-0.50 grams per cubic centimeter (g/cm^3) which, compared to the density for PBI polymer of 1.34 g/cm^3 results in an apparent void volume of 89-63% respectively.

2. Strength

Strength data was obtained by cutting a 1.5 cm wide strip with a JDC Precision Tensile Strip Cutter through the selected area. Often, this strip was weighed and the basis weight and densities calculated from it. Tensile testing was done on an Instron Universal Testing Machine with a 2.54 cm (1 inch) gauge length and a strain rate of 100% per minute. A strip tensile strength was then calculated in g/cm. To obtain tensile strength, the thickness of the strip adjacent to the break was determined and was used for the calculation.

3. Porosity

Porosity was determined by two methods, one of which is an air permeability test, ASTM D726B (Gurley). This test has been in use at Celanese for some time to characterize porous structures.

In this test, the time in seconds for a known volume of air to pass through the sample under a fixed pressure is determined. Thus a porous sample gives a low reading (called Gurley seconds), whereas a dense sample gives a high reading. Obviously, any defects in the sample also lead to lower values. On the other hand, this test is quick, dry, and non-destructive. In this way, it is well suited for quality control.

The other test used was a bubble pressure test in which the pressure required to cause a visible bubble of nitrogen to pass through the mat with a 2 cm head of 40% aqueous KOH solution was determined. For this test, a 2.54 cm (1 inch) diameter sample was cut from a mat with a die and was allowed to soak overnight in 40% aqueous KOH. For testing, it was assembled into a 2.54 cm (1 inch) diameter Gelman disk filter holder with a perforated support screen on both top and bottom. The bottom was then connected to a pressure gauge and a nitrogen pressure regulator. Ten ml of 40% aqueous KOH was then poured on top of the disk and the pressure under the sample was increased until bubbles appeared. The pressure at which that occurred is the bubble pressure.

4. Electrical Conductivity

This was measured on a specimen which had been immersed in 40% aqueous KOH overnight. The sample was clamped between two methacrylate blocks which serve as half cells with 40% aqueous KOH as the electrolyte, and the conductivity calculated from a measurement of the resistance of the cell to a 40 milliampere (mA) current flow.

RESULTS AND DISCUSSION

A. Initial Scouting

Fibrids are produced by the coagulation of a polymer solution or dope in a non-solvent under conditions of sufficient shear to attenuate and break up the resulting polymer strand. While there are many possible variables in the process, simple scouting experiments were done by injecting polymer dope from a hypodermic syringe into a Waring blender of coagulant.

Polymer dope was made from a small quantity of polymer on hand (21818-6(P915A)) by refluxing it for several hours with dimethylacetamide (DMAc) containing 2% LiCl. This dope was filtered through coarse paper to remove the undissolved granular polymer. Dope viscosity was 1.2 poise (Brookfield Model RVT No. 2 spindle at 20 rpm) with 9.1% solids as determined by precipitation, washing, and drying. It was known from prior experience that the solubility of PBI is a function of temperature, with 210-220°C being necessary to dissolve the entire polymer. By dissolving at reflux (165°C), only the lower molecular weight fractions were being dissolved. However, at the initial stage of the project, polymer molecular weight was not thought to be a significant variable.

Lithium chloride is normally added to PBI dope as a stabilizer to prevent "phase-out" or aggregation of polymer into a semi-solid mass. While certainly necessary for the stability of high solids dope, it may not be required for the low solids dopes generally used for preparing fibrids.

Initial experiments were done by injecting this dope into a rapidly stirred Waring blender containing the coagulant. Addition rates were slow enough and dilution rates were large enough so that polymer precipitation and mechanical shear produced fibrids. Microscopic examination of the resulting suspension was made, along with filtration and drying of the samples.

Several coagulants were tried. Water, both hot and cold, produced clumpy particles with low aspect ratios. Air entrainment caused the fibrids to float. Methanol produced particles similar in appearance to those produced in water, but no flotation occurred and handling was better. Coagulation in acetone produced fine, nice-looking fibrids. Upon filtration and drying, the mat shrunk and fused into a curled

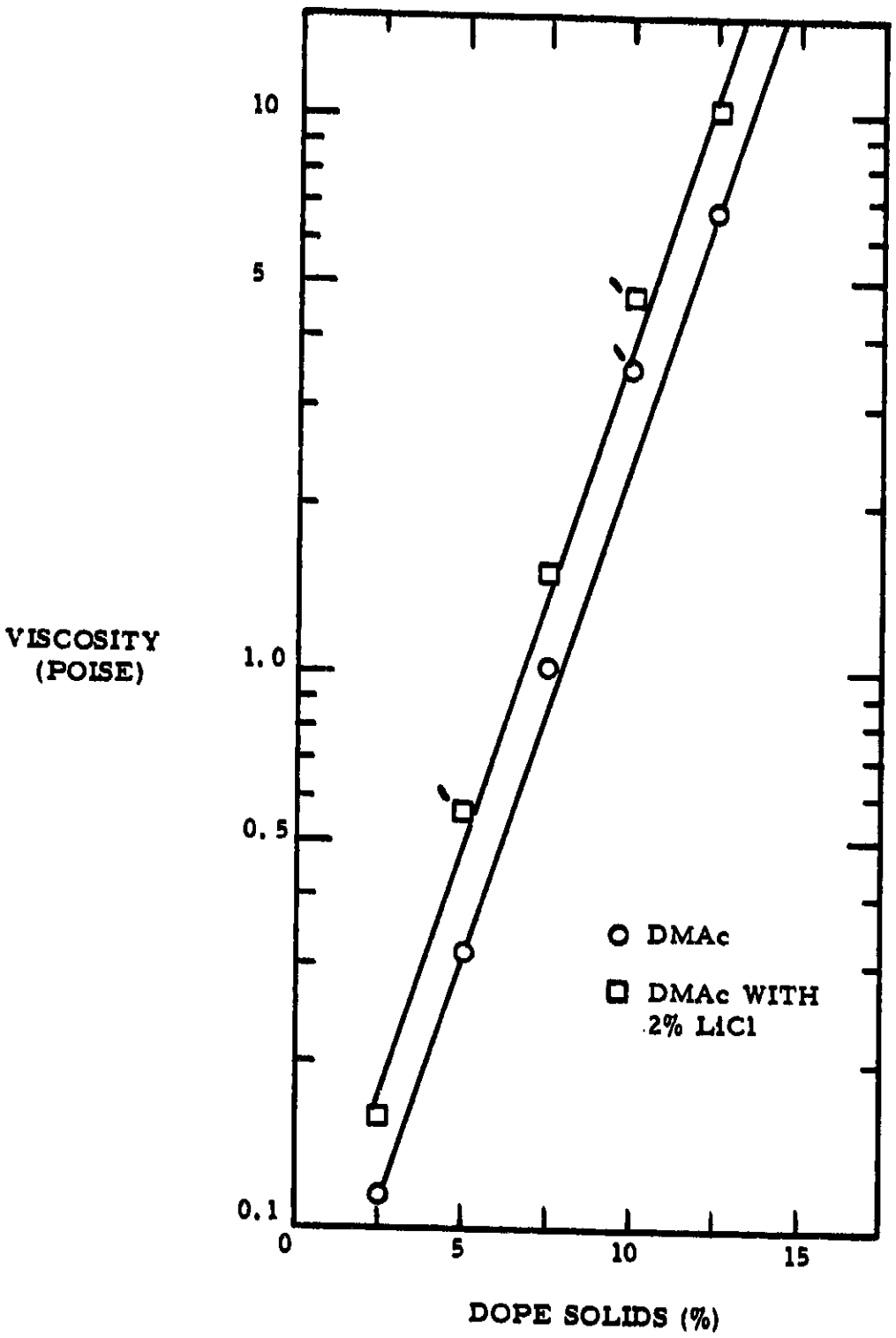
wafer, presumably due to residual DMAc remaining in the fibrids. Several washing steps with either acetone or boiling water before drying eliminated that problem.

Using methylene chloride, a different type of fibrid was produced which was more "rod-like" and tended to contain long fibers. This material also needed rewashing to prevent fusion on drying. The possible use of organic solvents as coagulants did not appear to be a significant disadvantage relative to water since recovery of the DMAc must be done in a plant for economic and environmental reasons.

Additional PBI dopes were made at different concentrations and viscosities by dilution of recovered PBI spinning dope with DMAc. Although the spinning dope contains LiCl as a dope stability additive, no additional LiCl was added upon dilution since it is unnecessary at the low solids concentrations used for fibrid preparation. While the presence of LiCl increases the viscosity of PBI dope, as shown in Figure 1, no effect of LiCl on fibrid formation was expected. Experiments were done with 5, 7.5 and 10% solids dopes and mixtures of DMAc/H_2O from 70/30 to 0/100.

Five percent dopes would not produce a strand, but rather formed drops which were subsequently chopped up into lumps. The 7.5 and 10% dopes did form strands, but they appeared to coagulate before they were suitably attenuated even in the 70/30 DMAc/H_2O mixture. Samples precipitated into higher contents of DMAc contained more fines, however, coagulation of the strand was still too rapid to allow the shear field to attenuate the dope. Slowing the coagulation rate and increasing the shear rate was necessary.

With these difficulties in mind, it was felt wise to experiment with other types of equipment. A fibrid apparatus was available for experimental trials elsewhere in the Corporation. This consists of a paint spray type jet with a pump to force the PBI dope through the center passage. A second pump and heat exchanger system allowed high pressure hot or cold water to be pumped through the air passages of the jet. An internal mix type cap was used with the resulting fibrids being sprayed into a 55 gallon drum. This process produced fibrids which appeared upon first examination to be in the micron-size range. At Summit, these fibrids were boiled with water to remove residual DMAc and were filtered to provide crude mats which had sufficient integrity to be handled. Slurries of this material in water were non-settling overnight; indicative of fine particle size.



Flagged points were obtained by dilution of sample. Other points represent a separate sample for each concentration.

Figure 1. - DOPE VISCOSITY OF PBI IN DIMETHYLACETAMIDE WITH AND WITHOUT 2% LiCl

Mats were formed by filtration of an aqueous slurry, using a laboratory fritted glass funnel overlaid with a sheet of Whatman No. 1 filter paper. Severe shrinkage and curling of the filtered mat occurred during unrestrained drying. However, drying between sheets of filter paper under pressure yielded flat and easily handleable mats. Shrinkage was calculated at about 22%, as measured by the change in average diameter. The density of this sample was 0.45 g/cm^3. Since the density of PBI is 1.3, a 65% void volume was calculated.

Characterization involved the measurement of porosity by air flow and bubble pressure, as well as, electrical resistance in 40% KOH. Asbestos mats, both neat and coated with PPO were received from NASA-Lewis and used as controls. As shown in Table I, the PBI mats seemed rather impermeable and had a high electrical resistance. The high bubble pressure found for the asbestos mat was believed due to sample compression in the apparatus. Bubble pressures were run on a sample which had been air dried, cut to size, soaked in 40% KOH, and assembled into the apparatus. Initially, the apparatus was incapable of measuring above 0.22 mega Pascals (MPa).* However, the region of interest was well below that, in the range of the asbestos samples. Electrical resistance measurements required soaking the mats overnight in 40% KOH in order to wet out the samples sufficiently to test, except in the case of the untreated asbestos which seemed to disintegrate. The high resistance found for the PBI mats was indicative of a low permeability material. Microscopy of both the fibrids and the mat was then done. Figure 2 shows a scanning electron micrograph (SEM) of some fibrids deposited on a metal plate. Some rod-like material is evident along with some film or sheet-like structures. When formed into a mat (Figures 3 and 4) a dense structure was obtained which seemed to contain significant quantities of sheet-like material.

B. Fibrid Preparation

A spray type fibrid apparatus was set up as shown in Figure 5. In addition to varying the fluid flow rates, the heat exchanger allows control of the coagulating water temperature. Higher temperatures should produce finer fibrids. Changes in coagulating liquid composition were taken care of by blending solvent (e.g. DMAc) and water in a 200 l (55 gal.) drum and feeding this mixture to the pump through a bypass valve to allow starting with water and then shifting to solvent.

In the initial experiments, the water (coagulant) pressure seemed to be the controlling factor in fibrid size. Dope pressure is a function of flow rate and is not an independent

* 1 MPa = 10^6 Newton/sq. meter = 145 psi

TABLE I. - CHARACTERIZATION OF INITIAL PBI MATS

Sample	Thickness (mm)	Thickness (mil)	Air[1] Flow Gurley (sec)	Bubble[2] Pressure (MPa)	Bubble[2] Pressure (psi)	Electrical Resistance[3] (m-ohm cm^2) 15 min.	Electrical Resistance[3] (m-ohm cm^2) Overnight
25536-14-1	0.25	(10.3)	∞	>0.22	(>32)	-	-
25536-14-2	0.41	(16)	∞	-	-	(4)	1410
25536-21-1	0.28	(11)	∞	-	-	(4)	1051
asbestos[5]	0.28	(11)	8.6	0.15	(22)	10.6	disintegrated
asbestos[5] coated with PPO	0.28	(11)	10.8	0.07	(10)	(4)	642

(1) ASTM D-726B

(2) Measured with a 1-inch diameter sample in 40% KOH. Apparatus could not exceed 0.22 MPa due to rubber hose connections.

(3) Measured in 40% KOH.

(4) Off Scale

(5) Received from NASA Lewis.

Figure 2. - SEM of PBI Fibrids on a Metal Surface

Figure 3. - SEM of PBI Fibrid Mat 25536-14-1

PBI Membrane 25536-14-1
500X X-sec 22 10/76

Figure 4. - SEM Cross Section of PBI Mat 25536-14-1

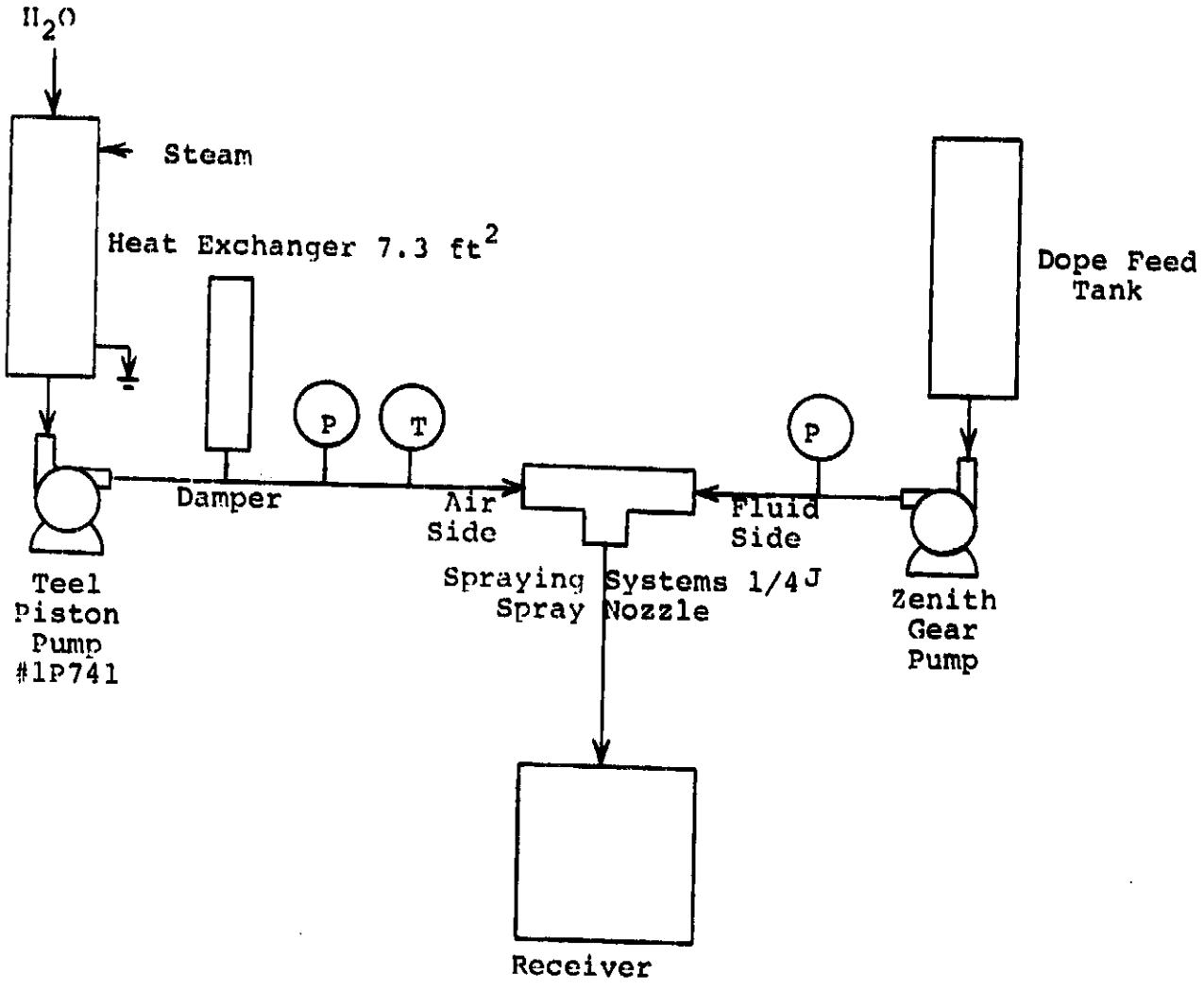


Figure 5. - Spray Apparatus

variable. This system tended to produce flat sheet-like fibrids which produce mats which are of low permeability. At lower water pressures, however, a greater amount of fibrous material was noted.

Samples were thoroughly washed in warm water before mats were formed. Analysis of the original mother liquor showed about 2.5% DMAc content. As noted before, mats were formed by filtration in a fritted glass funnel. They were air dried between sheets of filter paper and were weighted sufficiently to prevent curling. These results, shown in Table II, demonstrated that this system is capable of yielding fibrids which can produce both highly porous and relatively non-porous mats with simple changes in operating conditions.

Sample 25536-38-1, which produced a mat with a 3 Gurley sec airflow, was characterized by SEM. Figure 6 shows the surface of this particular mat, while Figures 7a and 7b show a cross section of this mat. It seems that sample 38-1 is quite similar in appearance to sample 14-1 even though its permeability is significantly greater. It is evident from these pictures that even though the airflow and bubble pressure of 38-1 show a highly porous material, the mat consists predominately of sheet like structures. Some of the fibrillar looking material is really the folded edges of sheet or web structures.

The SEM cross sections show a highly porous structure, not unlike the view seen when a cabbage is sliced. It would seem that the porosity of this sample results from the folding and packing of very thin sheet-like fibrids instead of the more conventional rod-like forms generally encountered in other polymer systems.

Additional experiments were done to explore the relationship between various operating parameters of the fibrid apparatus. Of particular interest was the coagulant (water) pressure, which seemed to be the most significant variable in previous tests.

As shown in Table III, the air permeability (Gurley) was found to be directly proportional to the coagulant pressure with relatively small pressure differences causing large permeability variations. Coagulant temperature made no apparent difference over the limited range studied. Operation with higher coagulant temperature proved impossible due to pump cavitation. Location of the heat exchanger downstream of the pump to eliminate this problem was not possible since the heat exchanger had an insufficient pressure

TABLE IIa. - CHARACTERIZATION OF PBI FIBRIDS

Sample[1] 25536-38-	Dope			Coagulant[2]			
	Flow Rate (ml/min)	Pressure (MPa)	(psi)	Temp. (°C)	Pressure (MPa)	(psi)	Flow Rate (l/min)
-2	73	0.34	(49)	60	0.47	(68)	1.94
-5	82	0.34	(50)	61	0.72	(105)	1.93
-6	82	0.38	(55)	64	0.76	(110)	2.18
-1	73	0.36	(52)	52	0.72	(105)	2.39
-8	82	0.62	(90)	65	0.83	(120)	2.73
-7	82	0.69	(100)	65	1.14	(165)	3.08

[1] Prepared with nozzle 2050 with internal mix cap 73160

[2] Water

TABLE IIb. - CHARACTERIZATION OF PBI FIBRIDS

	Mats						
Sample[1] 25536-38-	Thickness (mm)	(mil)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)	Elec. Resistance (m-ohm cm^2) Overnight	6 days
-2	0.84	(33)	0.1	<0.021	(<3)	139	139
-5	1.42	(56)	0.1	-	-	-	-
-6	0.91	(36)	0.3	-	-	-	-
-1	0.76	(30)	3.0	0.028	(4)	110	780
-8	0.94	(37)	6.0	-	-	857	-
-7	0.61	(24)	800	>0.22	(>32)	1614	573

[1]Prepared with nozzle 2050 with internal mix cap 73160

Figure 6. - SEM of 3 Burley PBI Mat

a. 75X

b. 750X

Figure 7. - Cross Section of 3 Gurley PBI Mat

TABLE III. - CHARACTERIZATION OF PBI FIBRID PROCESS

Sample[1] 25536-43-	Dope			Coagulant				Mats		
	Pressure (MPa)	(psi)	Rate Flow (ml/min)	Temp. (°C)	Pressure (MPa)	(psi)	Flow Rate (l/min)	Thickness (mm)	(mil)	Air Flow Gurley (sec)
-3	0.37	(54)	77	17	0.76	(110)	2.32	1.14	(45)	0.8
-4	0.33	(48)	76	47	0.78	(113)	2.34	1.09	(43)	1.2
-2	0.39	(56)	74	18	0.90	(130)	2.54	0.53	(21)	32
-5	0.37	(53)	77	47	0.90	(130)	2.53	0.71	(28)	34
-6	0.34	(49)	77	44	1.03	(150)	2.70	0.56	(22)	98
-1	0.39	(57)	76	19	1.07	(155)	2.81	0.36	(14)	>8000

[1] Made with nozzle 2050 and internal mix cap 73160

rating. All the mats were made with the same amount of slurry and contained approximately the same weight of solids, although the thicknesses varied threefold. After air drying for a week, all mats retained a moisture content of 12-13%. This was expected and is typical for PBI fibers. These fibrids were made with the same nozzle as was sample 38-1, thus it was expected that the mats obtained from this series of experiments would also have sheet-like structures, similar to that of 38-1.

Such sheet structures were presumed to be formed because the water impinges on the dope stream at an angle prior to the exit from the internal mix spray nozzle. Modifying the nozzle to have 6 rather than 3 feed holes for the coagulant was tried in order to present a more uniform radial pressure profile to the dope stream. No difference in performance could be seen between the two nozzles. In order to extrude the dope into a more nearly rod-like form, it was thought better to use a concentric external mix nozzle where the dope could be injected into the center of the coagulant stream. In this way, the coagulant stream would be expected to exert shear on the dope in a direction more nearly parallel to the axis of the flowing polymer solution. Furthermore, the coagulation rate might be retarded sufficiently to permit additional extension of the dope in the axial direction.

A suitable cap was obtained which met these criteria. The first series of experiments with this set up is summarized in Table IV. Microscopic examination revealed, however, that the resulting fibrids were still substantially flat rather than round.

Modifications to the fibrid apparatus were made to provide more stable pressures in the feed streams and to reduce pump cavitation. Figures 8 and 9 show the spray nozzles and the apparatus, respectively.

With this system upgrading completed, additive characterization of both the internal and external mix type nozzles was done. Fibrids made with the external mix nozzle were much coarser than those made with the internal mix nozzle. The external mix nozzle does, however, produce a more rounded fibrid. Internal mixing seemed to produce more turbulence and delivered a significantly greater coagulant flow rate at any given pressure than did external mixing. This is graphically shown in Figure 10.

TABLE IV. - FIRST FIBRIDS FROM EXTERNAL MIX NOZZLE

Sample[1] 25689-3-	Dope			Coagulant[2]			Mats[3]		
	Pressure (MPa)	(psi)	Flow Rate (ml/min)	Pressure (MPa)	(psi)	Flow Rate (l/min)	Thickness (mm)	(mil)	Air Flow Gurley (sec)
-4	0.12	(17)	35	1.59	(230)	1.65	0.43	(17)	66
-1	0.32	(47)	75	1.72	(250)	1.33	-	-	-
-2	0.32	(47)	75	2.07	(300)	1.82	-	-	-
-3	0.12	(17)	35	2.07	(300)	1.81	0.18	(7)	875

[1] System consisted of nozzle 2050 with external mix cap 64

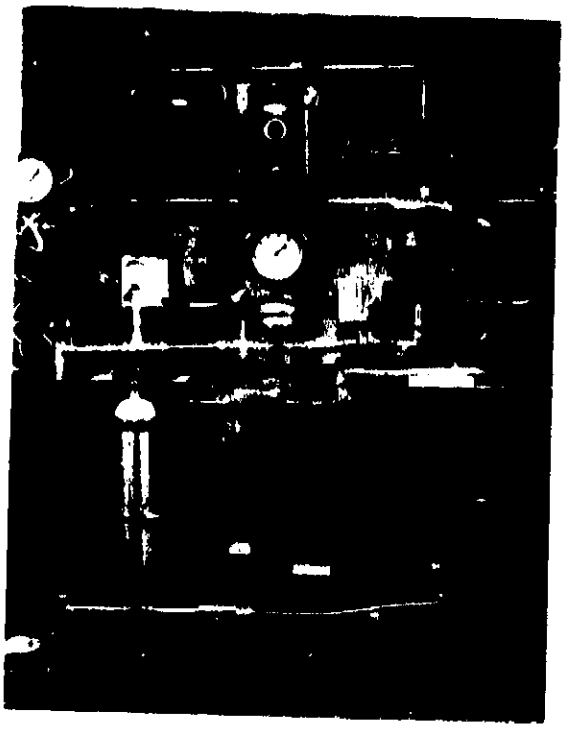
[2] Water temperature 24-26°C

[3] Mats fabricated directly from initial fibrid slurry

a. Internal Mix Nozzle

b. External Mix Nozzle

Figure 8. - Mix Nozzle



a. Overall View

b. Spray Nozzle in Operation

Figure 9. - Fibrid Apparatus

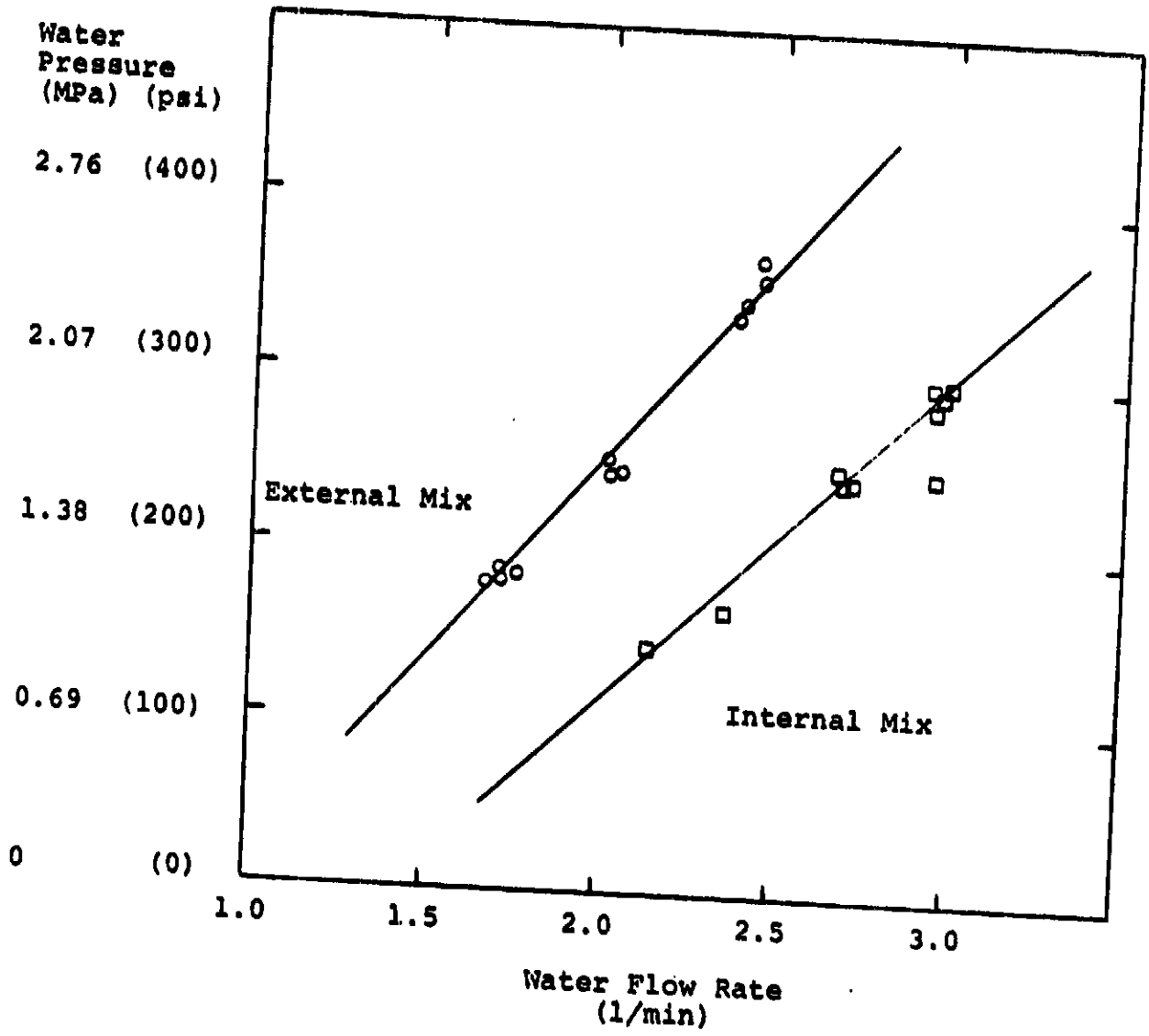


Figure 10. - Flow Rate Comparison of Nozzles

Data collected from an experiment where both nozzles were used is shown in Tables V and VI. The fibrids resulting from the conditions shown in Table V were formed with the external mix nozzle and appeared to be fibrous or rod-like. Increased coagulant pressure (and corresponding flow rate) yielded finer fibrids. On the other hand, all of these samples were coarser than were the samples obtained under the conditions reported in Table VI which were made with the internal mix nozzle. Equipment limitations with the external mix nozzle prevented higher pressure operations to further reduce fibrid size. Mats made from this series of experiments with the external mix nozzle were coarse, fibrous, and too porous to allow bubble pressure measurements within the desired 0.14-0.21 MPa (20-30 psi) range for fuel cell separators.

Samples in Table VI are listed in the order of increasing coagulant pressure which appears to be related to "fineness". Due to the heterogeneous nature of the fibrids, microscopic examination of the samples was tedious and subjective. Rather, visual observation could rank the samples into an order which correlates with the coagulant pressure. Coarse samples such as those resulting from the external mix conditions in Table V sank in the jar, while fine ones entrained sufficient air so that they floated. Thus, flotation and settling characteristics allowed sample ranking.

Half gallon sized samples were obtained which provided sufficient solids so that mats could be made on a 12.8 cm fritted glass filter. All of these mats were formed directly from the original fibrid slurry. One water rinse was given to each mat after formation but it was undoubtedly insufficient to completely remove all of the DMAc solvent. Mats were blotted and allowed to air dry while under a weight between sheets of filter paper. Wrinkling occurred at the edges, thus all measurements were made near the center. These mats resemble a strong, light brown, coarse paper in appearance and feel.

Permeabilities of the samples produced under the conditions shown in Table VI were obtained by both Gurley (air flow) and bubble pressure measurements. Circular samples (2.54 cm) were die cut for bubble pressure measurements and were soaked in 40% aqueous KOH overnight. The pressure limit for the apparatus (a Millipore filter holder) was 0.21 MPa due to the use of rubber tubing for making connections. The limited bubble pressure data, however, does show some correlation with the Gurley air flows and highlights the samples of interest.

TABLE V. - PBI FIBRIDS MADE WITH EXTERNAL MIX NOZZLE[1]

Sample 25689-17-	Dope[2] Pressure (MPa)	(psi)	Flow Rate (ml/min)	Coagulant[3] Pressure (MPa)	(psi)	Flow Rate (l/min)
-1	0.19	(28)	27.7	1.21	(175)	1.66
-2	0.19	(28)	27.7	1.21	(175)	1.71
-7	0.33	(48)	43.4	1.24	(180)	1.74
-3	0.21	(30)	27.7	1.65	(240)	2.01
-4	0.21	(31)	27.7	1.72	(250)	2.00
-8	0.33	(48)	43.4	1.65	(240)	2.04
-9	0.33	(48)	43.4	1.65	(240)	2.04
-10	0.33	(48)	43.4	2.28	(330)	2.36
-5	0.22	(32)	27.7	2.34	(340)	2.38
-11	0.33	(48)	43.4	2.52	(365)	2.44
-6	0.25	(36)	27.7	2.55	(370)	2.57

(1) Nozzle 2050, cap 64 - Spraying Systems Co., Wheaton, Illinois

(2) PBI dope - 11.6% solids in DMAc, 4.1 poise @ 25°C (Brookfield RTV - #1 @ 10 RPM)

(3) Water 12 - 13°C

TABLE VIa. - PBI FIBRIDS AND MATS MADE WITH INTERNAL MIX NOZZLE[1]

Sample 25689-17-	Dope[2] Pressure (MPa)	(psi)	Flow Rate (ml/min)	Coagulant[3] Pressure (MPa)	(psi)	Flow Rate (l/min)
-21	0.28	(40)	33.7	0.97	(140)	2.11
-16	0.31	(45)	42.3	1.10	(160)	2.33
-17	0.26	(38)	33.7	1.62	(235)	2.69
-18	0.28	(41)	33.7	1.62	(235)	2.68
-12	0.32	(47)	42.0	1.65	(240)	2.65
-13	0.34	(49)	42.3	1.65	(240)	2.93
-19	0.32	(46)	33.7	1.93	(280)	2.93
-20	0.32	(47)	33.7	1.96	(285)	2.91
-14	0.34	(49)	42.3	1.96	(285)	2.97
-15	0.34	(49)	42.3	1.96	(285)	2.95

(1) Nozzle 2050, cap 73160 - Spraying Systems Co., Wheaton, Illinois

(2) PBI dope - 11.6% solids in DMAc, 4.1 poise @ 25°C (Brookfield RTV - #1 @ 10 RPM)

(3) Water 11 - 12°C

TABLE VIb. - PBI FIBRIDS AND MATS MADE WITH INTERNAL MIX NOZZLE[1]

Sample 25689-17-	Mats[4] Thickness (mm)	(mil)	Air Flow Gurley (sec)	Bubble Pressure[5] (MPa)	(psi)
-21	0.25	(10)	1.6	0.021	(3)
-16	0.38	(15)	1.8	0.069	(10)
-17	0.20	(8)	68	>0.21	(>30)
-18	0.20	(8)	30	>0.21	(>30)
-12	-	-	-	-	-
-13	0.28	(11)	94	0.14	(20)
-19	-	-	-	-	-
-20	0.20	(8)	93	>0.21	(>30)
-14	0.20	(8)	132	>0.21	(>30)
-15	0.38	(15)	87	>0.21	(>30)

(1) Nozzle 2050, cap 73160 - Spraying Systems Co., Wheaton, Illinois

(4) Mats were formed on a 12.5 cm diameter fritted glass funnel and were washed once with water. All DMAc was not removed.

(5) Bubble pressure in 40% aqueous KOH. Samples soaked overnight. Pressure limit of apparatus is 0.21 MPa (30 psi).

C. Preparation of Low Shrinkage Mats

Early mats were made directly from the original fibrid suspensions. These generally contained about 0.2% PBI fibrids in water. Depending on the relative flow rate of the dope and coagulant, it was estimated that there was from 1 to 1.5% dimethylacetamide in this aqueous suspension. Each mat was rinsed with water after it was formed. However, it is known that PBI holds DMAc tenaciously and it is highly unlikely that a simple rinse was sufficient to remove the solvent completely. One relatively easy technique for DMAc removal is by washing the fibrids or mats with hot water. In the laboratory, this was readily accomplished by boiling the samples in water.

A specimen from sample 25689-17-21, (Table VI) which made a mat with 0.021 MPa (3 psi) bubble pressure, was boiled four times in water. Expectations were that it would become more porous and this was shown by samples -31-2A and -2B in Table VII. Additional mats were made of slurry -17-21 (-31-1A) which have similar properties to those reported in Table VI. In addition, to test rewettability, a sample was filtered to form a damp mat and then was redispersed in water and again formed into a mat. In this way, it was expected to simulate a process in which wet fibrids were stored and later reslurried to make mats. As is shown in Table VII, the unboiled sample, containing residual DMAc, did show a reduction in porosity due to the additional dispersing operation. The presence of residual solvent could also be involved, since the fibrids could be in a somewhat swollen state. By contrast, little change was noted when the fibrids had been boiled in water and presumably no longer contained residual solvent.

The most outstanding result of the boiling operation was to produce softer mats which were somewhat more fragile and lighter in color than the unwashed mats. This softness may be due to a reduction in adhesive bonding which the residual DMAc may effect during mat drying along with reduced bulk density due to the low shrinkage. In any event, mat shrinkage upon drying was reduced in half when the fibrids were treated so as to remove solvent. The boiling water treatment presumably causes a certain amount of preshrinkage to occur, thus alleviating the shrinkage problem that takes place during the drying of the mats.

TABLE VII. - FIBRID TREATMENTS

Sample 25689-[1]	Treatment	Thickness (mm)	(mil)	Density (g/cm^3)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)	Diameter (cm)	Shrinkage (%)
-31-1A[2]	None	0.41	(16)	0.29	1.0	0.021	(3)	10.3	17.5
-1B	Redispersed	0.36	(14)	0.34	8.5	0.034	(5)	10.3	17.5
-2A	Boiled in Water	0.46	(18)	0.21	0.3	0.021	(3)	11.5	8.0
-2B	Boiled in Water and Redispersed	0.36	(14)	0.22	0.3	0.014	(2)	11.5	8.0

[1] Made from fibrid 25689-17-21

[2] Duplicate of 25689-17-21 (Table VI)

SEM's of these mats, both cross sections and face views are shown in Figures 11-13. The mat made directly from the fibrid slurry (-31-1A) is typical of mats made previously. The surface has an overall "skinned" look due to the residual solvent and the deswelling and shrinkage which occurs on drying. These samples are relatively stiff compared to washed samples. Taking a damp mat, redispersing it in water with a Waring blender, and then forming a new mat does not significantly change the appearance of the mat as revealed in Figure 12. Boiling of the fibrids in water several times to remove residual solvent and to densify the fibrids prior to making a mat, significantly changes the surface of the mat producing a more open structure. In addition to making a more porous structure, the mats were softer and exhibited only 8% shrinkage upon drying, only about half as much as the unboiled samples.

Two larger fibrid samples were made using the internal mix nozzle and the same PBI dope as before. Conditions were chosen based on samples 25689-17-16 and -13 which gave bubble pressures of 10 and 20 psi respectively (Table VI). Five gallon size samples were taken (only about 2.5 gallons can be collected because of foaming) which allowed work-up of several aliquots. As shown below, calculated water flows for these longer timed samples are not consistent with water pressures or with the flows obtained previously for smaller very short timed runs. On the other hand, these high flow rates are consistent with later experiments and certainly reflect the greater accuracy of measurement obtainable with a larger (longer timed) sample.

Sample	Dope			Coagulant		
	Pressure		Flow Rate (ml/min)	Pressure		Flow Rate (l/min)
	(MPa)	(psi)		(MPa)	(psi)	
25689-35-1	0.43	(63)	44.9	1.10	(160)	3.73
-2	0.52	(75)	45.5	1.65	(240)	3.59

In addition to boiling these samples to remove DMAc, both were azeotropically distilled with toluene to "dry the fibrids" and to provide the maximum preshrink as well. While some agglomeration occurred during this process, dispersion in a Waring blender was sufficient to break it up. Loose fibrids were allowed to air dry overnight and were found to be readily redispersed in water to form mats. Properties

a. Cross-section 200X

b. Face 50X

Figure 11. - Mat 25689-31-1A Made Directly From Fibrid Slurry.

25689-31-1B

200X 2/3/77

a. Cross-section 200X

25689-31-1B Side B

50X 2/3/77

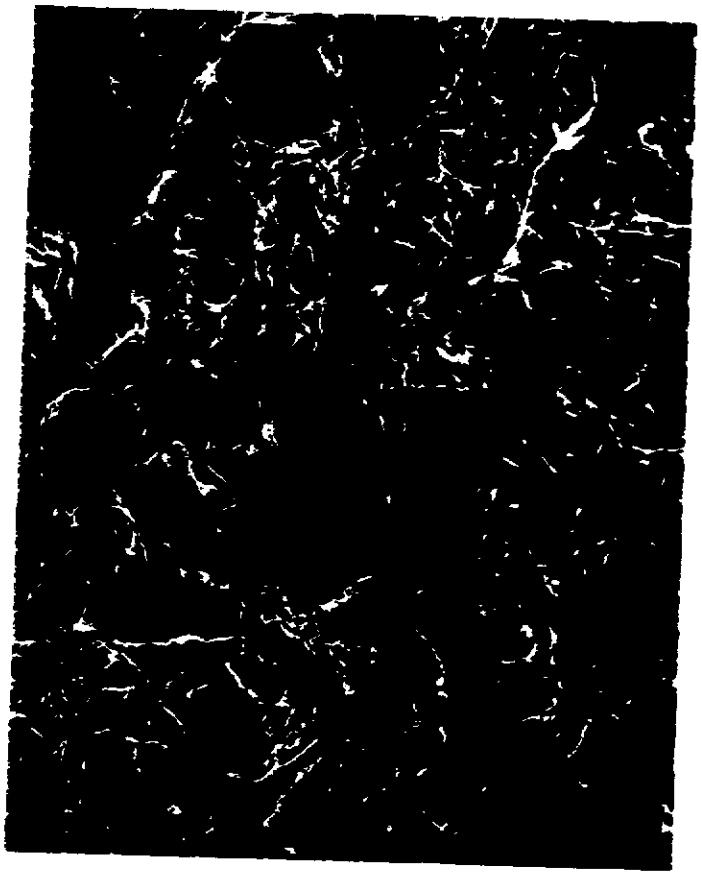
b. Face 50X

Figure 12. - Mat 25689-31-1B Made from Redispersed Fibrids

25689-31-2A

200X 3/77

a. Cross-section 200X



25689-31-2A Side A

50X 3/77

b. Face 50X

Figure 13. - Mat 25689-31-2A Made From Fibrids Boiled in Water

of mats made from each stage of the sample are shown in Table VIII.

SEM's of mats made directly from the slurry look like Figure 11. Samples which were boiled also looked similar to Figure 11 rather than to Figure 13 as expected. Shrinkages were found to be similar to the -31 series, 18.4% vs. 17.5% for the direct slurry samples and 10 vs. 8% for the boiled samples. The azeotropic dewatering with toluene reduced the shrinkage to 1% and produced very soft supple samples as shown in Figures 14 - 17. Mats made from fibrids -35-1 appear coarser than mats made from fibrids -35-2. (Compare Figure 14 and 15 with 16 and 17.) This was expected since the coagulant pressure for -35-2 was higher, 1.65 vs. 1.10 MPa (240 vs. 160 psi), however, the bubble pressure data show no difference. It was thus shown to be feasible to produce a "dry" fibrid which could be redispersed in water to make mats which can be dried with little shrinkage. However, the "drying" processes do increase the porosity and lower the density of the mats, an effect which must be compensated for during fibrid preparation.

The remainder of sample 25689-35-2, which had not been made into mats, was boiled in four changes of water, slurried with toluene and the water azeotropically removed, filtered and oven dried. Pictures of this dry fibrid sample, re-numbered 25689-41, are shown in Figure 18. This material was easily redispersed in water to form a slurry suitable for making mats.

Since both samples -35-1 and -2 produced mats with low bubble pressures, another fibrid run was made to prepare additional samples at higher water pressure. Except for the water pressure, conditions for making 25689-43-1 and -2 were the same as for -35 -2. Samples -43-1 and -2 were combined, boiled with water, azeotroped with toluene, filtered and air dried. A finer internal mix water cap was used to prepare samples -43-3 and -4 in hopes of obtaining even greater shear during fibrid formation and thus form finer fibrids. The finest external mix nozzle and cap were also tried (-43-5 and -6) in order to evaluate their performance. Table IX shows the conditions used.

Mats were made from each of these materials. Mats at three different weights were also made from each of the dried fibrid samples, -41 and -43-(1,2). Two 2.54 cm disks were cut from each sample, one to measure the bubble pressure

TABLE VIII. - SEQUENTIAL FIBRID TREATMENT

Sample 25689-	Treatment	Thickness (mm)	(mil)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)	Diameter (cm)	Shrinkage (%)
35-1[1]	As Made	0.38	(15)	2.5	0.021	(3)	10.2	18.4
	Boiled in Water	0.41	(16)	1.0	0.021	(3)	11.2	10
	Boiled in Water +toluene	0.66	(26)	1.0	0.007	(1)	-	-
35-2[2]	As Made	0.15	(6)	600	>0.14	(>20)	10.2	18.4
	Boiled in Water	0.33	(13)	18	0.021	(3)	11.3	10
	Boiled in Water +toluene	0.66	(26)	1	0.007	(1)	12.4	1
	Boiled in Water +toluene dried, redispersed in H_2O	0.36	(14)	1.5	0.021	(3)	-	-

[1] Duplicate of 25689-17-16 1.10 MPa (160 psi)

[2] Duplicate of 25689-17-13 1.65 MPa (240 psi)

25689-38-1A

50X 25 3/77

a. 50X

25689-38-1A

200X 25 3/77

b. 200X

Figure 14. - Mat From Sample 25689-35-1, Boiled With Water And Azeotroped With Toluene.

25699-38-1B
50X
26 3/77
a. 50X

25699-38-1B
1000X
26 3/77
b. 1000X

Figure 15. - Same Material as Figure 14, Except Fibrids Air Dried And Redispersed In Water.

25689-38-2A

50X

a.

27 1/77

50X

25689-38 2A

1000X

b.

27 3/77

1000X

Figure 16. - Mat From Sample 25689-35-2. Boiled With Water And Azeotroped with Toluene.

25689-38-2B

50X

28 3/77

a. 50X

25689-38-2B

1000X

28 3/77

b. 1000X

Figure 17. - Same Material As Figure 16. Except Fibrids Air Dried and Redispersed in Water.

a. Sample 25689-41 (from 25689-35-2) 1000X

b. Sample 25689-41 (from 25689-35-2) 50X

Figure 18. - SEM Of Dry Fibrids

TABLE IX. - PBI FIBRID SCOUTING

Sample 25689-43-	Dope Pressure (MPa)	Dope Pressure (psi)	Dope Flow Rate (ml/min)	Water Pressure (MPa)	Water Pressure (psi)	Water Flow Rate (l/min)
-1[1]	0.71	(103)	46.8	2.00	(290)	3.90
-2	0.55-0.83	(80-120)	47.6	2.00	(290)	3.89
-3[2]	1.02	(148)	46.6	1.76	(255)	2.70
-4	1.02	(148)	46.6	2.14	(310)	2.98
-5[3]	0.92	(133)	45.6	2.14	(310)	1.85
-6	0.88	(128)	46.4	2.69	(390)	2.21

(1) Samples 1 and 2 were combined. Made with internal mix nozzle 2050 with 73160 cap.

(2) Samples 3 and 4 were made with the same nozzle as above but with a smaller cap, (67417) hence the lower water flow rate.

(3) Samples 5 and 6 were made with the smallest external mix nozzle and cap (1650, 64).

and the other to obtain drying and moisture regain data. These samples were dried at 150°C at 10 mm Hg and then allowed to equilibrate in a 50% RH laboratory. From this data, the moisture content, as originally air dried, was calculated along with the moisture regain and the dry density. This data is shown in Tables X and XI. Improved accuracy can be obtained by using larger samples.

Table X shows that although -43-(1,2) should be finer than -41, and the mat densities upon air drying confirm a slightly more dense structure for -43-(1,2), the bubble pressure and air permeability tests (Gurley) do not show much difference. Table XI shows that -43-4 made at high pressure with a fine water cap produces a high density, high bubble pressure mat while the external mix nozzle samples, -43-5 and -6, produce very low density low bubble pressure mats as expected. It must be noted that all the samples in Table XI were made from the original suspensions and would be expected to produce more porous mats after being boiled, azeotroped, and dried.

In order to further characterize fibrid formation, washing, and azeotroping, sample 25689-43-5 was analyzed for its DMAc content and was then washed with water and azeotropically dried with toluene. Another sample of the same fibrid was simply azeotroped with toluene omitting the water washing step.

As shown in Table XII, the fibrid slurry, as made, contains about 2% DMAc, almost evenly divided between the solid and liquid phases. The water washing followed by azeotropically drying left a toluene slurry which contained only 0.15% H_2O with a very low level of DMAc. After filtration and air drying, the fibrids were found to contain 0.8% DMAc.

This concentration of residual DMAc is probably typical of the "dry" fibrids which we have been producing even though this is a coarse sample. A permissible level of residual solvent would have to be defined compatible with end use performance. In the fuel cell application, for example, it is not known whether DMAc acts as a poison and, if it does, whether there is a concentration below which the catalyst would no longer be adversely affected. If necessary, extensive washing with water can be expected to reduce the residual level substantially. When the water wash was omitted and the fibrids simply azeotroped, the DMAc level of the air dried fibrids was 1.8%, close to the original value. Washing with several changes of toluene might remove the DMAc solvent.

TABLE Xa. - EVALUATION OF FIBRID MATS MADE FROM DRY FIBRID SAMPLES

Sample 25689-	Thickness (mm)	(mil)	Density (g/cm^3)	Shrinkage on Drying (%)
-41	0.23	(9)	0.19	0
	0.33	(13)	0.22	4
	0.38	(15)	0.25	0
-43-(1,2)	0.23	(9)	0.22	4
	0.33	(13)	0.26	6
	0.38	(15)	0.28	6

TABLE Xb. - EVALUATION OF FIBRID MATS
MADE FROM DRY FIBRID SAMPLES

Sample 25689-	On 2.54 cm Disks: Air Dried Moisture Content (%)	Moisture Regain (%)	Dry Density (g/cm^3)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)
-41	45	5.2	0.17	4.5	0.055	(8)
	24	9.3	0.20	8.1	0.069	(10)
	28	7.2	0.19	3.9	0.055	(8)
-43-(1,2)	22	5.7	0.16	2.6	0	(0)
	27	10.3	0.19	11.3	0.083	(12)
	13	9.3	0.18	9.2	0.083	(12)

TABLE XIa. - EVALUATION OF MATS FROM 25689-43[1]

Sample 25689-43-	Thickness (mm)	(mil)	Density (g/cm^3)	Shrinkage on Drying (%)
-3[2]	0.28	(11)	0.26	16
-4[2]	0.23	(9)	0.35	14
-5[3]	0.58	(23)	0.11	2
-6[3]	0.46	(18)	0.14	8

[1] Mats were prepared from the original fibrid slurries.

[2] Internal Mix, 2050 with Fine cap 67147

[3] External Mix 1650 with 64 cap

TABLE XIb. - EVALUATION OF MATS FROM 25689-43[1]

Sample 25689-43-	On 2.54 cm Disks: Air Dried Moisture Content (%)	Moisture Regain (%)	Dry Density (g/cm^3)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)
-3[2]	18	6.6	0.22	3.6	0.021	(3)
-4[2]	33	7.8	0.30	144	0.10	(15)
-5[3]	11	6.9	0.12	<1	0	(0)
-6[3]	14	4.2	0.19	<1	0.021	(3)

[1] Mats were prepared from the original fibrid slurries.

[2] Internal Mix, 2050 with Fine cap 67147

[3] External Mix 1650 with 64 cap

TABLE XII. - WASHING OF FIBRIDS

Sample	Treatment	DMAc Content (%)	H_2O Content (%)
25689-43-5			
Liquid	As made	2.3	-
Solid	As made	2.0	-
25946-1B Liquid (toluene)	Above boiled H_2O-4X Azeotroped with toluene	N.D.	0.15
25946-1B Solid	Air dried solid from above	0.8	-
25946-1C Liquid (toluene)	25689-43-5, not H_2O washed Azeotroped with toluene	0.08	0.18
25946-1C Solid	Air dried solid from above	1.8	-

Two additional samples were washed and dried to provide mats for characterization. Sample 25689-43-6 was the finest sample made using the external mix nozzle configuration. As reported in Table XI, it gave a bubble pressure of 3 psi and appeared to be the type of porous open material desired for the alkaline battery separator. This sample, -43-6, was water washed and azeotropically dried from toluene. Two mats were then made, one with no aftertreatment, the other rolled with a steel calender roll to compact it. As shown in Table XIII, the calendered sample was found to have a somewhat higher density and bubble pressure than the other (un-calendered) sample, along with greater apparent strength. It seems to be similar to the Pellon 2506 reference sample in permeability.

Dry fibrids were also prepared from 25689-43-4 which was made using the standard internal mix fluid nozzle, along with a small cap at high pressure to produce high shear. Two mats were made with the original slurry, one was calendered, the other was not. As expected, the calendered sample was somewhat more dense with a greater bubble pressure. Both of these samples wrinkled upon drying.

Mats produced from dried fibrids prepared from -43-4 were less dense and had a lower bubble pressure than those prepared from the fibrid slurry. Calendering seemed to be more effective in compacting this sample (-21D) than for the sample made directly from the slurry (-21B). Neither of these mats made from dry fibrids wrinkled upon drying. These results are shown in Table XIV.

The large fibrid sample 25689-43-1,2 was washed 4 times with water and azeotropically dried by distillation with toluene. The resulting dry fibrid was relabeled 25689-44. A 14 gram sample of dry fibrid was shipped to NASA-Lewis to make high bubble pressure mats for evaluation in fuel cels. From these fibrids, mats were prepared for calendering studies. The first of these was made in the normal fashion while another was calendered to reduce its thickness by 5 mils. A third mat was made in order to experiment with different calendering procedures, redispersing the mat for each trial.

It is apparent from Table XV that multiple redispersings of this mat have not been deleterious. This demonstrates that recovery and reclamation of undried mats should present minimal problems provided that the sample is thoroughly rewetted before being dispersed.

TABLE XIII. - EVALUATION OF LOW BUBBLE PRESSURE MATS

Sample[1]	Thickness (mm)	(mil)	Density (g/cm^3)	Basis Weight (g/m^2)	Shrinkage Air Drying (%)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)
25946-17A	0.61	(24)	0.10	61	1	0.1	<0.0069	(<1)
25946-17B (Calendered)	0.48	(19)	0.12	58	0	0.1	0.0069-0.021	(1-3)
Pellon2506[2]	0.18	(7)	0.36	63	-	0.3	0-0.021	(0-3)

[1] These mats were produced from sample 25689-50 which was a washed and azeotropically dried sample of 25689-43-6.

[2] Supplied as a reference by NASA-Lewis.

TABLE XIV. - EVALUATION OF CALENDERED MATS

Sample	Thickness (mm)	Thickness (mil)	Density (g/cm^3)	Basis Weight (g/m^2)	Shrinkage Air Drying (%)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	Bubble Pressure (psi)
25689-43-4 (Table XI)	0.23	(9)	0.35	-	14	144	0.10	(15)
25946-21A (thin repeat of above)	0.15	(6)	0.31	47	11	34	0.062	(9)
25946-21B (as 21A but Calendered)	0.14	(5.5)	0.33	46	14	74	0.076	(11)
25946-21C (from 25689-43-4 fibrids, washed, dried)	0.25	(10)	0.19	49	5	1.1	0.041	(6)
25946-21D (as 21C but Calendered)	0.19	(7.5)	0.27	52	1	14	0.090	(13)

TABLE XVa. - EVALUATION OF DRY FIBRIDS FOR FUEL CELL APPLICATION

Sample[1] 25946-14-	Thickness (mm)	(mil)	Density (g/cm^3)	Basis Weight (g/m^2)	Shrinkage Air Drying (%)
-1	0.36	(14)	0.19	67	3
-2 (-14-1-Calendered)	0.23	(9)	0.29	66	4
-3 (Redispersed and calendered several times)	0.25	(10)	0.25	58	2

Dry Calendered Samples			
25946-14-1	0.23	(9)	0.29
25946-14-2	0.15	(6)	0.38
25946-14-3	0.15	(6)	0.43

[1] All Samples made with dry fibrids 25689-44 produced from 25689-43-1,2

TABLE XVb. - EVALUATION OF DRY FIBRIDS FOR FUEL CELL APPLICATION

Sample[1] 25946-14-	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)	Tensile[2] Strength (MPa)	(psi)
-1	4.4	0.041	(6)	1.20	(174)
-2 (-14-1-Calendered)	40	0.14	(21)	3.03	(440)
-3 (Redispersed and calendered several times)	25	0.069	(10)	2.16	(314)

Dry Calendered Samples		
25946-14-1	0.076	(11)
25946-14-2	0.21	(30)
25946-14-3	0.069	(10)

(1) All samples made with dry fibrids 25689-44 produced from 25689-43-1,2

(2) Tensile strip of 15 mm wide, 50.8 mm jaw spacing, 200%/min extension. Elongation was 3%.

A typical procedure for mat making was as follows: For a 12.5 cm round mat, about 0.75 g of dry fibrids were added to about 500 ml of water and allowed to soak for an hour. They were then dispersed at high speed for 3 minutes in a Waring blender. The mat was formed by filtering this slurry through a 12.5 cm coarse fritted glass funnel. After removal from the funnel, the mat was blotted dry with filter paper. If calendered, it was passed several times between a set of rolls with the mat being sandwiched between filter paper. Drying was again done between filter paper using sheets of plywood with a 4 kg weight on top to keep the mat flat.

After drying the mats, they were equilibrated at 50% RH overnight and were then weighed and measured; the Gurley air flow determined and a 15 mm strip cut for a tensile test. From the remainder, a 2.54 cm diameter disk was cut and soaked overnight in 40% KOH before obtaining a bubble pressure. These samples exhibited a tensile strength sufficiently high to ensure easy handling. In fact, the properties of sample 14-2 seem to fit the requirements for the fuel cell mat; i.e., low shrinkage, 0.23 mm (9 mil) thick, 0.14 MPa (21 psi) bubble pressure with a 3.03 MPa (440 psi) tensile strength.

The grips on the tensile tester compressed the samples to 0.15 mm (6 mil) thickness. Consequently we took another piece of each dried mat and compacted it dry with the calender rolls. This again raised the bubble pressure. It thus appears that either wet or dry calendering or a combination thereof will facilitate production of PBI mats from dry fibrids with the desired properties.

Another larger sample of PBI fibrids, similar to 25689-44 which was sent to NASA-Lewis, was prepared. Table XVI shows data for this as well as for three other samples which were made at the same time to explore once again other nozzle cap combinations. Nozzle No. 1650 is smaller than the normally used 2050, while cap 67147 is smaller than the normally used 73160. Thus we tried a system with the standard nozzle but a smaller cap (as we had with 25689-43-3; Table IX) at similar pressure expecting to attain greater shear during the fibrid preparation. Using a smaller nozzle should make a smaller fibrid, and using the smallest nozzle with the maximum coagulation pressure attainable was expected to produce the finest possible fibrids which could be made with an external mix nozzle on the system.

TABLE XVI. - PREPARATION OF PBI FIBRIDS

Sample[1] 25946-29-	Spray[2]		Dope[3]			Water[4]		
	Nozzle	Cap	Pressure (MPa)	(psi)	Flow (g/min)	Pressure (MPa)	(psi)	Flow (l/min)
-1,2,3,4[5]	2050	73160	0.76	(110)	42.6	2.00	(290)	3.86
-5,6	2050	67147	1.03	(149)	44.6	2.07	(300)	2.62
-9,10	1650	67147	1.03	(149)	45.1	2.24	(325)	3.04
-7,8	1650	64	1.02	(148)	45.5	2.59	(375)	2.39

(1) Data shown are averages for all of the samples made at those conditions.

(2) All spray combinations are internal mix except for 1650/64 which is external.

(3) Dope viscosity, 4 poise, ∿10% solids.

(4) Water temperatures, 14-15°C.

(5) Repeat of 25689-43-1,2 (dried as 25689-44)

Each of these samples was washed free of DMAc with boiling water and was then dried by slurrying with toluene and azeotropically distilling the water from them.

Properties obtained from the mats made from these four fibrid samples are shown in Table XVII. Both calendered and uncalendered mats were prepared. As noted previously, calendering increases mat density, strength, and bubble pressure. The density data reported were calculated based on the size and weight of the tensile strip. Tensile strengths in both SI and English units have been calculated from the original data, not converted just from one to the other. The tensile data were taken in grams on a single 15mm strip. Strip tensile data is included since it is a more accurate number (due to variability in measuring thickness of a compressible sample) and is useful for papers and fabrics. Elongations, while not tabulated, ran about 3-4%.

No particular advantage of the various nozzle-cap combinations over the standard one can be seen from the data. In fact the standard nozzle produced fibrids (25946-29, -1,2,3,4) which made the strongest and least porous mat of the three, contrary to our predictions that the other fibrids samples would be finer and would thus have better properties.

The fibrids made with the external mix nozzle (-7,8) were found to be too coarse and short to produce a mat with sufficient handling strength to test. Blending of these with finer fibrids, however, might be a method producing lower bubble pressure mats for the alkaline battery separator application.

D. Low Bubble Pressure Mats

Since it appeared that a fine dry fibrid could be produced which could be made into mats and calendered to prepare high bubble pressure mats for fuel cell separators, a shift in focus was made to the preparation of fibrids with low bubble pressure suitable for producing alkaline battery separators. Sample 25689-35-1, which was described and characterized in Table VIII, seems to fulfill the low bubble pressure requirements. Although a washed sample of 35-1 was available, a new fibrid sample was made of sufficient size so that a number of replicate mats could be made. In addition to the sample for the alkaline battery separator, another sample was made using the conditions that would give a high bubble pressure as desired in the fuel cell application. Conditions for producing these samples are shown in Table XVIII.

TABLE XVIIa. - EVALUATION OF DRY PBI FIBRIDS[1]

Fibrids 25946-29-	Mat 25946-	Treat.[2]	Thickness (mm)	Thickness (mil)	Density (g/cm^3)	Basis Weight (g/m^2)
-1,2,3,4	36-1	-	0.35	(14)	0.18	64
-1,2,3,4	36-2	+	0.17	(6)	0.36	61
-5,6	38-1	-	0.51	(20)	0.13	68
-5,6	38-2	+	0.22	(9)	0.30	67
-9,10	38-5	-	0.10[3]	(4)	0.65	65
-9,10	38-6	+	0.15	(6)	0.43	64
-7,8	38-3	-	too fragile to test			
-7,8	38-4	+				

(1) Please see Table XVI for fibrid preparation conditions.

(2) + indicates a calendered sample, - indicates no treatment.

(3) Sample was severely tapered, thus strength and density data are unreliable.

TABLE XVIIb. - EVALUATION OF DRY PBI FIBRIDS[1]

Mat 25946-	Tensile Strength (MPa)	(psi)	Strip Strength (g/cm)	(#/in)	Airflow Gurley (sec)	Bubble Pressure (MPa)	(psi)
36-1	1.15	(165)	413	(2.31)	3.9	0.055	(8)
36-2	5.04	(796)	853	(4.78)	38.5	0.090	(13)
38-1	0.20	(28.6)	102	(0.57)	<1	0.0	(0)
38-2	0.78	(110)	177	(0.99)	1.6	0.048	(7)
38-5	0.80	(120)	87	(0.5)	<1	0.041	(6)
38-6	3.86	(548)	587	(3.28)	39.9	0.076	(11)

[1]Please see Table XVI for fibrid preparation conditions.

TABLE XVIII. - PREPARATION OF PBI FIBRIDS

Sample[1] 26084-2-	Dope Pressure (MPa)	Dope Pressure (psi)	Dope Flow Rate (g/min)	Dope Viscosity (poise)	Water Pressure (MPa)	Water Pressure (psi)	Water Flow Rate (l/min)	Remarks
-2,3,4[2]	0.43	(63)	47.5	4.1	1.17	(170)	2.33	Battery Separator
-5,6,7[3]	0.43	(63)	48.6	4.1	2.07	(300)	3.02	Fuel Cell
-8,9,10,11	1.03	(149)	48.3	25	2.00	(290)	3.03	Battery Separator-coarse fiber
-12-13	1.03	(149)	48.3	25	1.38	(200)	2.38	Very long coarse fiber

[1] All samples made with internal mix nozzle 2050 and cap 73160.

[2] A duplicate of 25689-35-1.

[3] A duplicate of 25946-29-1.

Samples were made under two different conditions with a higher viscosity dope (25 poise vs. 4.1 poise - approximately 15% vs. 10% solids). As expected, significantly longer fibrids were produced with the higher viscosity dopes. These may be useful for blending to improve the strength of mats made with finer fibrids.

These fibrids were worked up in the standard fashion by boiling with water to remove residual dimethylacetamide, and then azeotropically dried in toluene. Final drying was done in an oven. The resulting "Dry" fibrids were assigned notebook numbers 26084-3, -4, -5, -6 respectively.

Standard mats were made with 0.5 g of each of these fibrids on 12.5 cm filter paper. Of particular interest was the difference in mat properties between the fuel cell material, -4, and a slightly coarser varient, -3. The coarse fibrids, -5 and -6, made from the higher viscosity dope were considered of interest mainly for blending with the fine fuel cell material to increase porosity and strength while, at the same time, decreasing bubble pressure. Each of these samples was calendered while wet to a nominal 0.13 - 0.18 mm (5-7 mil) thickness. However these mats became somewhat thicker after drying. Visual inspection showed that mat -11-1 was of poor uniformity and that mat -11-4 was very weak probably due to the coarse fibrids.

Table XIX ranks the mats in order of increasing fibrid coarseness and shows that the coarser fibrids, -5 and -6, produce mats which have a lower bubble pressure and strength. Contrary to the original expectations, no particular advantage could be seen for the blended samples shown at the bottom of the table as compared with the others, although strengths are slightly higher. Additional mats were made with the fuel cell fibrids, -4, and the slightly coarser, -3, samples in order to determine the differences between them. All of these samples ended up quite thin and dense after calendering, leading to high bubble pressures. Again, as shown in Table XX, there is little difference between the two fibrids, suggesting that the fuel cell material may be suitable for both applications, calendering for high bubble pressure fuel cell mats and using a light weight uncalendered mat for alkaline battery mats.

A 9-inch square sheet mold was constructed with which to fabricate the requisite number of mats required to be delivered under Tasks III and IV. Initial mats made with this apparatus

TABLE XIXa. - PROPERTIES VS. FIBRID COARSENESS

Sample 26084-	Fibrid[1] 26084-	Thickness (mm)	(mil)	Basis Weight (g/m^2)	Density (g/cm^3)	Strip Strength (g/cm)
-11-2	-4	0.18	(7)	38	0.22	75
-11-1	-3	0.24	(9)	47	0.20	152
-11-3	-5	0.20	(8)	41	0.21	46
-11-4	-6	0.28	(11)	39	0.14	5
-12-1	60%-4	0.16	(6)	42	0.27	124
	40%-3					
-12-2	60%-4	0.16	(6)	36	0.22	81
	40%-5					
-12-3	60%-4	0.18	(7)	43	0.23	98
	40%-6					

[1] See Table XVIII for fibrid formation conditions. Fibrid -3 derived from fibrids-2-2, -2-3 and -2-4 after azeotropic drying. Similarly, -4 is the dried form from -2-5, -2-6 and -2-7; -5, the dried form from -2-8,-2-9, -2-10 and -2-11; -6 dried form from -2-11 and -2-12.

TABLE XIXb. - PROPERTIES VS. FIBRID COARSENESS

Fibrid[1] 26084-	Tensile Strength (MPa)	Bubble[2] Pressure (MPa)	(psi)	Air Flow Gurley (sec)	Electrical[3] Resistance (m-ohm cm^2)
-4	0.47	0.028	(4.0)	1.0	85
-3	0.55	0.024	(3.5)	1.6	123
-5	0.23	0.007	(1)	<1	86
-6	0.018	<0.007	(<1)	<1	-
60%-4	0.77	0.033	(4.8)	5.5	103
40%-3					
60%-4	0.50	0.020	(3.0)	1	61
40%-5					
60%-4	0.53	0.032	(4.6)	1.2	77
40%-6					

(1) See Table XVIII for fibrid formation conditions. Fibrid -3 derived from fibrids -2-2,-2-3 and -2-4 after azeotropic drying. Similarly, -4 is the dried form from -2-5, -2-6 and -2-7; -5, the dried form from -2-8, -2-9, -2-10 and -2-11; -6 dried form from -2-11 and -2-12.

(2) Bubble pressure measured on 2.54 cm disk in 40% KOH after overnight immersion.

(3) Electrical resistance determined in 40% KOH at 40 mA after overnight immersion.

TABLE XXa. - PROPERTIES OF ALKALINE BATTERY MATS

Sample 26084-	Fibrid[1] 26084-	Thickness (mm)	(mil)	Basis Weight (g/m^2)	Density (g/cm^3)	Strip Strength (g/cm)
-16-2	-3	0.17	(7)	45	0.39	270
-16-1	-3	0.09	(4)	41	0.46	153
-16-3	-3	0.11	(4)	33	0.32	11.6
-16-5	-4	0.09	(4)	36	0.40	191
-16-6	-4	0.09	(4)	36	0.39	217
-16-4	-4	0.10	(4)	28	0.30	95

[1]See Table XIX for fibrid preparation conditions.

TABLE XXb. - PROPERTIES OF ALKALINE BATTERY MATS

Sample 26084-16-	Tensile Strength (MPa)	Bubble Pressure[2] (MPa)	(psi)	Air Flow Gurley (sec)	Electrical Resistance[3] (m-ohm cm^2)
-2	2.3	0.11	(16)	43	122
-1	1.7	0.096	(14)	45	109
-3	1.1	0.061	(8.8)	4.7	72
-5	2.1	0.11	(16)	39	80
-6	2.3	0.028	(4)	27	62
-4	0.98	0.14	(20)	5	62

(2) Bubble pressure measured on 2.54 cm disk in 40% KOH after overnight immersion.

(3) Electrical resistance determined in 40% KOH at 40 mA after overnight immersion.

are characterized in Table XXI. The first mat shown in the Table, -14B1, turned out to be very thick and heavy. Since it was not calendered, the mat had a relatively low density. Bubble pressure and handling strength were reasonable. Half of this material was then dry calendered to compact it and was renumbered -14B2. Tensile strength, bubble pressure, and density of the calendered mat increased. The electrical resistance decreased slightly.

From these results, it was concluded that alkaline battery mats should be made with a basis weight of about 35 g/m^2. To test this conclusion, mat, -15, was made with half the quantity of the coarser (-3) fibrid as was the mat, -14B1. A large set of steel calender rolls was used to compact the wet mat before drying. Using similar conditions, mat, -17, was made from the fuel cell grade of fibrids (-4). Both of these mats were strong, of reasonable density, and possessed low electrical resistance. A high bubble pressure was obtained for mat, -17, as had been found previously (Table XX) for the -16 series of mats made from the finer fibrids. This was exactly what was desired for fuel cell use. It may be that less calendering could produce the required low bubble pressure alkaline battery mat from the fine fibrid. Conversely, preparation of high bubble pressure fuel cell mats by heavy calendering of mats made with the coarser fibrids may be a better choice.

A review of the data in Table XXI showed that fibrid 26084-3, made at 1.10 MPa (160 psi) coagulant pressure, was capable of producing mats with the requisite properties for alkaline battery separators. The mat made with the fine fuel cell fibrids (26084-4) which was made with 2.07 MPa (300 psi) coagulant pressure easily produced high bubble pressure mats as desired for fuel cells.

Attempts to produce lower bubble pressure mats from the fuel cell fibrids were not successful. As shown in Table XXII, five additional large mats were made from the -3 (1.10 MPa) fibrids, and two from the latest batch of -4 type (2.07 MPa) material. Again the measured properties of the mats made with the -3 fibrids fit the general criteria of bubble pressure and thickness desired. Samples 3A and 4A, respectively, represent portions of samples 3 and 4 which were dry calendered to reduce their thickness and increase sample density. The bubble pressure seems to have remained below 0.034 MPa (5 psi) target maximum.

TABLE XXIa. - EVALUATION OF LARGE ALKALINE BATTERY MATS

Sample 26084-	Fibrid[1] 26084-	Thickness (mm)	Thickness (mil)	Basis Weight (g/m^2)	Density (g/cm^3)	Strip Strength (g/cm)
-14B1	-3	0.70	(27)	78	0.11	138
-14B2	-3	0.25	(10)	74	0.30	173
-15	-3	0.12	(5)	33	0.28	158
-17	-4	0.12	(5)	37	0.31	225

(1) See Table XIX for fibrid preparation conditions.

TABLE XXIb. - EVALUATION OF LARGE ALKALINE BATTERY MATS

Sample 26084-	Tensile Strength (MPa)	Bubble[2] Pressure (MPa)	(psi)	Air Flow Gurley (sec)	Electrical[3] Resistance (m-ohm cm^2)
-14B1	0.19	0.016	(2.3)	< 1	204
-14B2	0.70	0.034	(5.0)	4	174
-15	1.3	0.033	(4.8)	10	80
-17	1.8	0.16	(23)	9	83

(2) Bubble pressure measured on 2.54 cm disk in 40% KOH after overnight immersion.

(3) Electrical resistance determined in 40% KOH at 40 mA after overnight immersion.

TABLE XXII. - PROPERTIES OF LARGE ALKALINE BATTERY MATS

Sample 26084-	Fibrid 26084-	Thickness (mm)	Thickness (mil)	Basis Weight (g/m^2)	Density (g/cm^3)	Bubble Pressure (MPa)	Bubble Pressure (psi)	Air Flow Gurley (sec)
-19-1	-3[1]	0.11	(4)	32	0.30	0.050	(7.3)	9-13
-2	-3	0.19	(7)	31	0.16	0.024	(3.5)	<1
-3	-3	0.29	(11)	30	0.10	0.014	(2.0)	<1
-3A		0.15	(6)	30	0.21	0.033	(4.8)	<1
-4	-3	0.37	(14)	35	0.10	0.021	(3.0)	<1
-4A		0.20	(8)	35	0.18	0.018	(2.6)	<1
-5	-3	0.19	(7)	30	0.15	0.038	(5.5)	<1
-22-1	-21A[2]	0.10	(4)	35	0.40	>0.21	(>30)	385-587
-2	-21A[3]	0.11	(4)	32	0.30	0.16	(23)	25-85

[1] Dry fibrid from 26084-2-(2-4) Table XVIII.

[2] A fuel cell fibrid 2.07 MPa (300 psi) water washed only.

[3] The same sample as -22-1 after being azeotroped and dried in the normal fashion.

Samples -22-1 and 2 were made with a new batch of fuel cell fibrids which should be comparable with the -4 fibrids used in the past. Mat -22-2 was made in the normal fashion and shows properties very similar to mat 26084-17 shown in Table XXI. The other mat, -22-1, was made with the same fibrids after they had been washed free of solvent but before they had been azeotropically dried. This experiment was performed in order to determine again the benefits of the azeotropic drying. A comparison of the data in Table XXII shows that the bubble pressure, air flow, and mat density were higher for the sample made from the non-azeotroped fibers. A major difference in shrinkage was found as expected, with the mat -22-2 being 11% smaller in area, after being dried, than -22-2. Besides shrinking more, sample -22-1 wrinkled excessively, even though it was restrained during drying. A sample of the water washed only fibrids (the same as was used to make -22-1) was oven dried instead of being azeotropically dried. After dispersal in water in a Waring blender, a hand sheet was made which had no strength, presumably a result of the blender chopping up the fibrids which had shrunk together during drying producing a powder-like product rather than a fibrid. These experiments confirmed prior observations and demonstrated that:

1. oven drying of water wet fibrids produces a solid mass incapable of redispersion.

2. mats produced from water swollen fibrids tend to wrinkle and shrink excessively, and

3. a superior process results when the water washed fibrids are dried by azeotropic distillation to shrink them without excessive entanglement followed by filtration of the fibrids from the toluene with removal of residual toluene by air or vacuum drying.

This process provides a dry, clumpy fibrid which can be easily soaked and redispersed in water to be wet-formed into mats.

To provide additional fibrids for fuel cell development another large batch of material was made under the same conditions as previous samples (26084-4 was the last fuel cell sample made). As had been requested by NASA, deionized water was used rather than city water for making and processing these fibrids in order to ascertain the amount of

inorganic impurities retained by the fibrids. The deionized water conductivity was checked prior to processing and was found to be 0.5 megohm. A portion of the resulting fibrids was ashed and analyzed by emission spectroscopy along with 26084-6, a previously prepared fibrid which was made from the same PBI dope but processed with city water. As shown in Table XXIII, the ash levels are nearly the same. City water, as expected, gave higher levels of calcium and magnesium but for some unexplained reason, high phosphorous and silicon levels were noted in the sample treated with deionized water. What possible effect these impurities would have on mat end use is unknown.

During the processing of this batch, it was noted that, if the fibrids were very wet when charged into the kettle for azeotropic drying, they tended to clump up into beads. These proved to be capable of being dispersed in water (mat 26084-22-2 was made from them) but procedures to produce a fibrous rather than a bead product are preferred. After drying, 329 g of fibrids were obtained of which 135 g were sent to NASA for evaluation.

E. Scale-up

Scale-up of the process to allow the preparation of larger quantities of fibrids for both fuel cells and alkaline batteries was begun. This effort was required in order to provide for a purchase order from NASA which called for

1. 41.8 m^2 (50 yd^2) of PBI fibrid alkaline battery mat, and

2. a sufficient quantity of fuel cell grade dry PBI fibrids to produce 41.8 m^2 (50 yd^2) of mat.

To accomplish this, the fibrid formation equipment was set up in the pilot plant with fibrid deionized water slurry sprayed into a tank and then drained by gravity to a centrifuge for separation. A 1500 l (400 gal.) jacketed stainless steel vessel was used for the four deionized water washes, again collecting the fibrids with the centrifuge. Azeotropic distillation was also done in this vessel using about 625 l (165 gal.) of toluene after which the slurry was centrifuged and the fibrids allowed to air dry. After the bulk of the toluene had evaporated, the fibrids were dried in an oven at 75°C under 500 mm (20 in.) of reduced pressure.

TABLE XXIII. - ASH COMPOSITION OF FIBRIDS
PROCESSED IN CITY VS. DEIONIZED WATER

Sample	26084-6 (1)	26084-21A (2)
Ash(%)	0.79	0.71
Composition of Ash(%)		
B	0.1	0.5
Si	10	15
P	1	20
Mn	0.3	0.1
Mg	10	1
Pb	1	1
Sn	-	0.1
Fe	3	3
Cr	0.3	0.3
Ni	0.5	0.5
Al	4	2
Ca	30	2
Cu	1	1
Na	0.1	0.1
Zn	0.8	0.5
Ti	0.3	0.7
Sr	0.1	0.01

(1) Made and washed with Summit, N.J. city water.

(2) Made and washed with deionized water.

Two batches of PBI dope of approximately 75 l (20 gal.) each were prepared by redissolving PBI yarn. Preliminary small scale trials showed that this dope did not process in exactly the same manner as did previous dope, producing a somewhat finer material at any given pressure. Analysis of the polymer samples showed that the new dope had a higher inherent viscosity than the old dope and thus upon dilution in the same manner to a constant viscosity would have somewhat lower solids. We believe that lower dope solids was the cause of the observed finer fibrids. However, before this problem was recognized 1120 g of dry alkaline battery fibrids were produced using the previous conditions of 0.10 MPa (160 psi) water (coagulant) pressure (used for -3).

Some of this material was used in preliminary trials on a laboratory scale paper machine. These trials were not completely successful in producing a continuous web because of machine limitations. However, the results did suggest that continuous sheet could be made under proper conditions. The results also served to show that this sample of fibrids (26084-26) was somewhat finer than the target material (26084-3). Upon screening various process conditions in the laboratory, a coagulant pressure of 1.03 MPa (150 psi) was determined as being the condition which would produce a product similar to 26084-3 with the available dope.

Kimberly-Clark Corporation had agreed to fabricate the 41.8 m^2 (50 yd^2) of alkaline battery separator mat. They evaluated some of these fibrids in hand sheets and felt that in order to provide sufficient web strength to handle in the machine, it was necessary to add 20% of a very fine PBI fibrid for a binder. This was prepared using a 70/30 blend of DMAc/H_2O as coagulant and was added as a wet slurry to the aqueous suspension of the coarser fibrids. These ultrafine solvent containing PBI fibrids had been developed as a route to an ultrathin paper structure which could be metallized to form the surface for the solar sail project. This work was supported by NASA-AMES under contract No. NAS2-9526[25]. The fine fibrids assist in entangling the coarser fibrids while the added DMAc may also provide some solvent swelling and bonding. Based on this feedback from Kimberly-Clark, the preparation of approximately 4.5 kg (10 lb.) of dry fibrids was begun along with a suitable quantity of the very fine fibrid slurry.

Pilot plant preparation of fibrids was done with a single spray nozzle in about 17 hours. Coagulation conditions were the same as for 26084-3 except that coagulant pressure was

1.03 MPa (150 psi) instead of 1.10 MPa (160 psi) as explained above. The dope flow rate averaged 47.7 g/min with a coagulant flow of 2.55 l/min.. This flow rate was checked periodically by collecting a two minute sample and weighing. After washing, azeotropically drying, and oven drying, 4040 g (8.9 lb.) of dry fibrids were obtained (26084-30).

To produce the fine fibrids, drums of 70/30 DMAc/H_2O were prepared and set up to allow a gravity feed with about a 2.5 m (8 ft.) head to the pump. The second batch of dope was used to prepare this sample which was made with the same spray system (2050 nozzle and 73160 cap) and the same dope flow rate (47.7 g/min.) as for the dry fibrids but with a coagulant pressure of 1.24 MPa (180 psi). Four 200 l (55 gal.) drums representing some 1120 g (2.5 lb.) of solids were collected (26084-32). Some settling and decantation was done to reduce the final shipping volume to 3 drums. In addition to the 4040 g of 26084-30, samples 26084-26 and -27 (made at 1.10 MPa (160 psi)) were blended in to yield a total of 4650 g (10.25 lb.) of dry fibrid, 26084-34, which was shipped to Kimberly-Clark Corporation for paper making trials along with 3 drums of 26084-32 fine fibrid DMAc/H_2O slurry. A portion of the dry -34 fibrids was retained at Celanese (635 g).

Kimberly-Clark Corporation prepared the alkaline battery mat for us. All actual paper making, of course, used city water. In order to provide adequate handling strength as evaluated by pretrial hand sheets, Kimberly-Clark added 20% of the fine -32 slurry (containing DMAc) to the water slurry of dry fibrids to produce the mat. Unfortunately, DMAc is very difficult to wash from PBI, and thus when the web reached the drying cans of the paper machine, the residual DMAc tended to fuse areas of the paper. The best of the samples were oven dried by Kimberly-Clark to remove residual DMAc (which could be smelled) and were then rewound into smooth rolls. Others were left in the as-made state. Folded scrap was returned to us along with 12 flat sheets, each of which contained some defects. Each sample was assigned notebook number 26084-48, and samples were obtained for analysis as shown in Table XXIV.

On the six rolls, only one Gurley and bubble pressure was determined with the exception of sample 5, where the very low bubble pressure resulted from edge leaks due to the somewhat stiff sample. Two of the 12-sheet samples were measured in four places. Two separate samples of the folded scrap were selected, soaked in water to soften them, and dried under weights. The results from these samples are also shown.

TABLE XXIV. - KIMBERLY-CLARK CONTINUOUS ALKALINE BATTERY MAT TRIAL

Sample 26084-48-	Form	Size (cm)	Comments	Thickness (mm)	Basis Weight (g/m^2)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)
-1	Roll	30 x 168	Smooth, 1 piece	.19 - .20	51	3.8	0.028	(4)
-2	"	30 x 326	Best, 1 piece	.18 - .19	38	4.7	0.045	(6.5)
-3	"	26 x 853	Smooth, 4 pieces	.12 - .18	41	4.7	0.028	(4)
-4	"	30 x 396	Wrinkled, 2 pieces	.15 - .16	54	66	0.11	(16)
-5	"	30 x 527	Wrinkled, 1 piece	.14 - .17	61	38	<0.007	(<1) [1]
-6	"	24 x 686	Wrinkled, 3 pieces	.09 - .12	59	76	0.083	(12)
-7	Sheet	25 x 25	Smooth	.11 - .14	42	1-6 [2]	0.014-0.033	(2-4.8) [2]
-8	"	25 x 25	Smooth	.11 - .12	43	4-6 [2]	0.041-0.055	(6-8) [2]
-9	Scrap	-	Re-wet, re-dried	.11 - .15	49	4-6 [3]	0.048-0.059	(7-8.5) [3]
-10	"	-	Re-wet, re-dried	.11 - .12	51	11-17 [3]	0.083-0.11	(12-16) [3]

[1] Two samples run; sample not flat enough to seal.

[2] Four samples run

[3] Two samples run

For unknown reasons, the smooth redried samples have a significantly lower bubble pressure than the wrinkled samples, although the amount of fusion seems similar. It appears that the first three rolls have suitable bubble pressures for the alkaline battery application, however, the aesthetics are quite poor. While somewhat disappointing, nonetheless, it must be remembered that this was the first trial of PBI fibrids on a continuous paper machine, and much was learned.

F. Larger Scale Fuel Cell Fibrids

To provide the required larger quantities of the fuel cell fibrid, some preliminary laboratory fibrid work up was done of samples made at different pressures. Calendered mats made from these materials and from retains of fuel cell fibrid 26084-21A had bubble pressures as shown in Table XXV.

Based on this data, a coagulant pressure of 1.90 MPa (275 psi) was selected for the preparation of this sample. The dope flow rate was the same as had been used for the alkaline battery fibrids, 47.7 g/min.. Deionized water was used as the coagulant and for washing. After washing, the solids level of the centrifuged cake was found to be 6.9%. After azeotropic distillation with toluene to dewater the fibrids, a solids level of 19.4% was found. A yield of 3740 g (8.25 lb.) was obtained after vacuum oven drying. This material was identified as 26084-47.

G. Evaluation of Alkaline Battery Material

Because of the marginal quality of the PBI paper made on the small scale continuous paper machine, it was considered to be unsuitable for use in the NASA battery building program. For this program, 250 six inch square sheets were required. Kimberly-Clark agreed to process these fibrids into handsheets using a 30 x 66 cm (12 x 26 in.) handsheet mold rather than to attempt another continuous roll trial which might have consumed a large quantity of fibrids. Preliminary sheets, made at 0.25 mm (10 mil) thickness, were then calendered to 0.18 mm (7 mil). Samples of these were sent to both Celanese and NASA-Lewis for testing.

Data on these preliminary sheets is shown in Table XXVI. NASA data and Celanese data generally agree except for the electrical resistance. In this case, the value determined

TABLE XXV. - FUEL CELL FIBRID SCOUTING

Sample	Thickness (mm)	(mil)	Air Flow Gurley (sec)	Bubble Pressure (MPa)	(psi)	Basis Weight (g/m^2)	Density (g/cm^3)
2.07MPa (300psi) trial	0.13	(5)	33	0.19	(27)	54	0.41
	0.16	(6)	12	0.23	(33)	65	0.41
1.90MPa (275psi) trial	0.17	(7)	15	0.16	(23)	56	0.33
	0.30	(12)	9	0.12	(17)	85	0.28
26084-21A	0.11	(4)	25	0.16	(23)	32	0.30

TABLE XXVI. - ALKALINE BATTERY HANDSHEETS (KC #799-65)

Sample 26374-1-	Basis Weight (g/m^2)	Thickness (mm)	(mil)	Density (g/cm^3)	Tensile Strength (1) (MPa)	(psi)	Strip Strength (2) (g/cm)	Bubble Pressure (MPa)	(psi)	Air Flow Gurley (sec)	Electrical Resistance (m-ohm-cm^2)
-1	51	0.19-0.22	(7.0-8.2)	0.25	1.66	(240)	315	0.026, 0.036	(3.8, 5.2)	2.4,2.5	132
-2	48	0.17-0.20	(6.3-9.0)	0.26	2.01	(292)	345	<0.007, 0.064	(<1, 9.3)	4.0,4.3	125
-3	50	0.21-0.23	(7.5-8.7)	0.22						2.2,2.3	
-4	47	0.19-0.20	(7.3-8.0)	0.24						3.0,3.0	
NASA	47-50	0.17-0.20	(7-8)					0.055	(8)		204,214

(1) 2.54 cm (1 in.) gauge length, 100%/min. extension, n = 4, 2 values one way, 2 perpendicular

(2) n = 4, 2 values one way, 2 perpendicular

by NASA was 50% higher than that found at Celanese. However, the higher value still was in an acceptable range.

After reviewing this data, it was decided to have Kimberly-Clark decrease the basis weight by 10 g/m^2. This should reduce the thickness to the 0.18 mm (7 mil) maximum desired as well as increase the porosity, thereby lowering the bubble pressure and electrical resistance.

During this period, a 30-day ageing test of a fuel cell mat in 40% KOH at 90°C was completed. Problems with the heating bath allowed some water loss with a consequent increase in the concentration of base. Nonetheless, although the sample was cracked from physical abuse, it had a bubble pressure of 0.041 MPa (6 psi) at the end of the test, as compared with 0.065 MPa (9.5 psi) at the start, which indicates that PBI fibrid mats are capable of withstanding long time exposure to hot concentrated alkali.

After reviewing with NASA the data on the preliminary handsheets prepared by Kimberly-Clark it was mutually agreed to use a new lot of fibrids from recently polymerized PBI polymer to prepare the handsheets for the alkaline battery separators. A standard batch (B-261) was made of 24% PBI dope in DMAc containing 2% LiCl from polymer P(2039-40-38)A. This was a typical PBI polymer with an inherent viscosity of 0.75 dl/g (0.4% in 97% H_2SO_4). Solutioning and filtration seemed normal in all respects. This filtered dope was then placed in a 200 l (55 gal.) stainless steel drum and was diluted in several steps to 5 poise.

A short scouting fibrid run was made with different pressures to explore the fibrid preparation condition response for this particular batch of dope. Samples made at 1.03 MPa (150 psi) and 1.90 MPa (275 psi) were selected as appearing best and were worked up by the standard procedures to provide a dry fibrid. A wet solids content, before azeotropically drying of 6.5 and 5.3% respectively was calculated. A 9 cm diameter mat from the 1.03 MPa (150 psi) material had a thickness of 0.26-0.29 mm (10-11.4 mil) and a Gurley Air Flow of 0.75 sec at a basis weight of 52 g/m^2. This seemed reasonable compared to previous alkaline battery mats such as shown in Table XXVI. The mat made from the 1.96 MPa (285 psi) sample had a thickness of 0.60-0.74 mm (23-29 mil) and a Gurley Air Flow of 1.1 sec at a basis weight of 103 g/m^2. While this is somewhat too porous, it was expected that calendering would bring this mat into the range for fuel cell application.

Preparation of the large sample for conversion by Kimberly-Clark into handsheets was then initiated. Over a period of 5 days, fibrids were made for 28 hours using the above 5 poise dope, the standard 2050-73160 nozzle-cap combination, 1.03 MPa (150 psi) of deionized water at 23-26°C, and a dope pressure of 0.28-0.48 MPa (40-70 psi) at a flow rate of 48.5 g/min. of dope. (The low dope pressure occurred on a day when the dope temperature was higher.) Every hour, a 3-minute sample was obtained and weighed in order to ensure that the system was operating in a stable and uniform manner. These samples weighed between 8.6 and 9.0 kg (19 and 20 lbs.). After washing with water, azeotropically distilling water from a toluene slurry, and vacuum drying, a yield of 10.4 kg (22.9 lb) of dry fibrid 26374-19 was obtained.

From the same dope, an ultrafine fibrid sample was prepared using a 70/30 mixture of DMAc/water for the coagulant. The apparatus was identical, except for a gravity feed of the DMAc-water mix through a valve to the feed pump, so arranged that the operation could be started using water as coagulant and then be shifted to the DMAc-water mix. Dope feed parameters were the same as before, but coagulant pressure was 1.55 MPa (225 psi) at a temperature of 36°C. Due to some operating difficulties,only 88.7 kg (195.5 lb.) of this slurry (26374-12) was collected. This slurry was placed into a stainless steel drum for shipment to the Schweitzer Division of Kimberly-Clark along with 6.8 kg (15 lb.) of the dry fibrids (-19).

From these fibrids, Kimberly-Clark again prepared five 30.4 cm square handsheets, three of which were sent to NASA for their evaluation while the other two were tested at Celanese.

The properties obtained are shown in Table XXVII. Sheets identified as 26374-20B, 26374-20C and 26374-20D were sent to NASA. The other two samples (A and E) were retained by Celanese.

Although the specifications (32 g/m^2 basis weight, 0.13-0.18 mm (5-7 mil) thick) were met, the strip strength reported by Kimberly-Clark (160 g/cm) was somewhat lower than in previous samples. The reason for the lower sheet strength was thought to be a consequence of a lower aspect ratio of the fibrids. These sheets were made with a nominal 20% of the fine fibrid 26374-12. Sheets

TABLE XXVII. - ALKALINE BATTERY HANDSHEETS (KC #818-54-2)

Sample 26374-	Weight (g/m^2)	Thickness (mm)	(mil)	Density (g/cm^3)	Strip Strength (g/cm)	Tensile Strength (MPa)	(psi)	Air Flow Gurley (sec)
-20A	33	0.13-0.15	(6)	0.23	161	1.04	(150)	2.8
-20B	32	0.16-0.17	(6)	0.20				2.1
-20C	32	0.15-0.18	(6)	0.20				1.5
-20D	33	0.14-0.15	(6)	0.22				1.7
-20E	34	0.14-0.17	(6)	0.22	178	1.14	(166)	1.7

26374-20A and -20E were analyzed for their DMAc content and were found to have 2.5 and 3.0% respectively. This was not unexpected since removal of DMAc from PBI by simple rinsing is difficult. Prior to use in a battery these mats should be thoroughly rinsed with water to remove DMAc and to wet out the mat.

When NASA tested these sheets in 45% KOH at 90°C, it was observed that they lost integrity after 12-24 hours. Assuming that this resulted from a physical loosening of the matted fibrids and was related to the relative weakness of the sheet, it was decided to target for a stronger and thicker mat. While this would give a heavier sheet, a post processing calendering could be done to meet a 0.18-0.20 mm (7-8 mil) thickness. Kimberly-Clark was asked to increase sheet strength by increasing the basis weight.

Kimberly-Clark found that mats of improved strength could be produced by using the earlier sample of "fine" fibrids (26084-32) which had been used in the continuous paper machine trial. Unfortunately this sample was stored in carbon steel drums and some rust formation occurred during this time. By careful selection, however, the iron was minimized. In addition to using these -32 fibrids, they also increased the basis weight of the sheet to 50 g/m^2 and used 30% of the fine fibrids rather than the 20% as used previously. The properties obtained on two small trial handsheets are shown in Table XXVIII. These properties agree with those reported by Kimberly-Clark. NASA-Lewis confirmed that these samples did not deteriorate and lose integrity in hot caustic as had the earlier ones. Electrical resistance was low and the bubble pressure was 0.028 MPa (4 psi).

Since the "old fine" fibrids seemed to contain some rust from the storage drums, it was desirable to determine the inorganic contaminants present. Half of one handsheet was aged for 18 hours in 45% KOH at 123°C, washed until neutral with hot deionized water, and then dried in vacuum. This sample was then analyzed by X-ray fluorescence spectroscopy along with the untreated, unwashed half. Both samples contain calcium, chlorine, sulfur, iron, chromium, and traces of titanium. In addition, the caustic-treated sample contained traces of nickel. Caustic treatment did seem to remove some of the iron and sulfur.

TABLE XXVIII. - KIMBERLY-CLARK BATTERY SEPARATORS

Sheets - 70% dry fibrid 26374-19
30% "fine slurry" 26084-32
KC #833-22-1

Sample	26374-41-1	26374-41-2
Basis weight (g/m^2)	49	51
Thickness (mm)	0.19	0.18
(mil)	(8)	(7)
Density (g/cm^3)	0.25	0.27
Strip Strength (g/cm)	161	218
Tensile Strength (MPa)	0.79	1.2
(psi)	(114)	(171)
Air Flow Gurley (sec)	-	1-3
Bubble Pressure (MPa)	-	0.028
(psi)	-	(4)

The detectable limit of the method is estimated to be on the order of 100 ppm. Iron and the stainless steel metals come from the processing equipment. It is known that PBI picks up alkaline and alkaline earth elements so that calcium pick-up from processing water was to be expected. Also, it was previously observed that PBI will, in effect, remove chlorine from water. The origin of the sulfur is not clear although some does exist in the original PBI polymer.

After consultation with the NASA Project Manager, it was decided to have Kimberly-Clark produce additional sheets identical to these to meet the contractual requirements.

Kimberly-Clark prepared 26 PBI fibrid hand sheets 30x65 cm (12x26 in.) suitable for alkaline battery separators which were delivered to NASA for evaluation. Properties of these sheets were:

Sample	27518-23-1 through -26 (KC #897-5-4)
Basis weight g/m^2	39-41 g/m^2
Thickness	0.16-0.20 mm (6.5-8.0 mil)
Strip strength g/cm	216

To complete the requirements of Task IV of the contract, 21 nominal 20x20 cm (8x8 in.) alkaline battery mats of about 35 g/m^2 basis weight were delivered. Properties of these sheets, made from fibrid 26374-19, are shown in Table XXIX. Under Task III, a number of denser mats, suitable for fuel cell matrices, were delivered. Two different lots of fibrids were used; 26084-34 which was the alkaline battery fibrid sample used by Kimberly-Clark in their continuous paper machine trial, and 26084-47 which was made and sampled to NASA-Lewis for fuel cell usage. Characteristics of these 21 mats are shown in Table XXX. The mats from -47 were made at a nominal 85 g/m^2 basis weight while those from -34 were made significantly heavier at about 115 g/m^2 since the -34 fibrid was coarser and would thus require greater compaction to yield a high bubble pressure material. All of these fuel cell samples were calendered to reduce their thickness to the 0.20-0.25 mm (8-10 mil) range.

To determine whether high bubble pressure mats suitable for fuel cell separators could be made from the alkaline battery 26374-19 fibrids, samples at three basis weights were prepared and then calendered while still wet to 0.20-0.23 mm (8-9 mil) thickness. The properties obtained with these samples are shown below:

C-2

TABLE XXIX. - ALKALINE BATTERY MATS[1]

Sample 27518-	Basis Weight (g/m^2)	Thickness (mm)	(mil)	Bubble Pressure (MPa)	(psi)	Air Flow Gurley (sec)
-8	37	0.25	(9.7)	0.017	(2.5)	1.1
-10-1	36	0.24	(9.6)			1.5
-10-2	35	0.20	(7.8)	0.028	(4.0)	0.1
-10-3	35	0.18	(7.0)			0.1
-10-4	35	0.20	(7.9)			0.2
-10-5	34	0.22	(8.6)			1.5
-10-6	33	0.19	(7.5)			0.2
-10-7	36	0.23	(9.0)			0.1
-11-1	34	0.23	(9.0)			0.1
-11-2	35	0.21	(8.3)			0.1
-11-3	37	0.22	(8.5)			0.1
-11-4	34	0.21	(8.3)			0.2
-11-5	36	0.21	(8.1)			0.1
-11-6	35	0.20	(7.8)			0.1
-11-7	35	0.20	(7.7)			0.1
-11-8	33	0.23	(8.8)	0.017	(2.5)	0.1
-11-9	35	0.17	(6.8)			0.3
-11-10	37	0.24	(9.5)			0.1
-11-11	35	0.26	(10.1)			0.1
-11-12	34	0.21	(8.2)			0.1
-11-13	35	0.20	(8.0)			0.2

[1] Delivered to NASA

TABLE XXX. - FUEL CELL MATS[1]

Sample 27518-	Basis Weight (g/m2)	Thickness (mm) (mil)	Bubble Pressure (MPa) (psi)	Air Flow Gurley (sec)
Fibrid 26084-47				
-15-1	87	0.22 (8.8)		30
-15-2	85	0.18 (7.0)		221
-15-3	87	0.18 (7.2)		129
-15-4	84	0.20 (8.0)		67
-15-5	84	0.22 (8.6)	0.21 (30)	30
-15-6	88	0.22 (8.5)		66
-18-5	88	0.23 (9.2)		7
-18-6	84	0.25 (9.8)	0.055 (8)	7
-18-7	87	0.24 (9.3)		9
-18-8	96	0.27(10.6)		18
-18-9	73	0.20 (8.0)		9
Fibrid 26084-34				
-13-1	117	0.24 (9.6)		268
-13-2	11	0.23 (9.0)	0.21 (30)	122
-13-3	122	0.18 (7.2)		5600
-13-4	117	0.23 (9.2)		281
-13-5	119	0.28(11.1)		107
-13-6	119	0.24 (9.4)		50
-18-1	101	0.33(12.9)		2
-18-2	102	0.33(12.8)		4
-18-3	94	0.30(11.8)		2
-18-4	92	0.30(12.0)	0.031 (4.5)	1

[1] Delivered to NASA

Sample		27518-22-1	27518-22-1	27518-22-3
basis wt. g/m^2		89	115	137
thickness mm		0.21	0.20	0.23
	(mil)	(8.3)	(7.9)	(9.0)
bubble pressure	MPa	0.12, 0.90	0.38, >0.41	0.31, >0.41
	(psi)	(18, 13)	(55, >60)	(45, >60)
air flow-Gurley	(sec)	26	62	460

It would thus appear that a sheet with a basis weight of about 100 g/m^2 appropriately calendered should produce the desired > 0.14 MPa (>20 psi) bubble pressure for fuel cell separators. Based on this, 1.0 kg (2.2 lb) of 26374-19 battery fibrids were shipped to NASA for future evaluation in fuel cell applications.

H. Alkaline Ageing of PBI Mats

After several different batches of PBI fibrids had been evaluated by NASA contractors, it became apparent that the resistance of PBI mats to hot concentrated caustic for long times was not as good as had been expected, based on data obtained on PBI textile yarns several years earlier and that different samples behaved somewhat differently. A major difference between the textile yarn and fibrids is that the textile yarn had been drawn (stretched) at a temperature of 450-500°C with a residence time of several seconds in air in order to improve its strength. During this drawing, some crosslinking occurs which renders the drawn textile fiber insoluble in DMAc, its original spinning solvent. A reasonable scenario is that this crosslinking of textile fiber contributes to the improved resistance to alkali. It was thus proposed to measure the weight loss of PBI mats in 45% KOH at 123°C (250°F) and then to evaluate suitable heat treatments for the fibrids or mats in order to improve their resistance to the hot caustic.

Washing and drying trials with loose fibrids quickly led to the conclusion that mechanical handling losses would be too great to allow generation of weight loss data. Thus, mats were made from fibrid 26374-19 (the same material sent to Kimberly-Clark to fabricate into mats) and these were used to generate base line weight loss data in 45% KOH at 123°C as well as in water at 55°C.

Small samples of mat, ~0.25 g, were placed into a closed stainless steel vessel with 45% KOH and were suspended in an oil bath at 123°C. The samples were removed after exposure, washed with hot (80°C) water until neutral, then given an additional rinse, and dried overnight at 130°C and 432 mm of vacuum. Upon comparison with the original oven dried weight, the weight loss was calculated. The sample was then returned to fresh 45% KOH and the cycle repeated. The following control data for fibrid 26374-19 were obtained which show aconsiderably greater loss in caustic as compared with water. (The water losses were assumed to be mainly mechanical.)

Time (hrs)	Cumulative Wt. Loss in H_2O @ 55°C (%)	Cumulative Wt. Loss in 45% KOH @ 123°C (%)
70.5	2.7	6.6
92.5	2.7	7.3
187.5	3.1	8.7

Samples of fibrid 26374-19 were treated in a static air oven for one hour at 250, 275, 300, 325, 350, and 375°C; and mats were then made from the 250°C and the 375°C samples. Whereas the 250°C sample made a normal mat, the 375°C sample lacked integrity. Microscopic examination revealed no difference in the fibrids other than a slight darkening. Another mat was then made from the 375°C treated fibrids after allowing them to swell in water overnight to ensure complete water absorption and plasticization. The resulting mat was much stronger than the earlier one leading to the conclusion that the heat treated fibrid samples are more difficult to rewet than untreated ones.

Two different approaches were tried: 1) Heat treat the fibrids and then produce a mat; and 2) fabricate the mat first and then heat treat it. Heat treatment darkens PBI somewhat, causes weight loss due to water desorption, and seems to cause some shrinkage and embrittlement. Thus the fibrid samples treated in the air oven were found to be more difficult to wet out in water than the original fibrids and, even after standing overnight in water, did not appear to form as nice, strong, or handleable a mat as did the original fibrids. Furthermore, alkali ageing seemed to affect the treated fibrids adversely.

In the second case, where mats were fabricated from the original fibrids and were then heat-treated, a useable mat remained, although somewhat more brittle and fragile than the untreated mat. For that reason, we concentrated mainly on heat treatment of mats rather than fibrids.

The initial experiments were done by fabricating a 12.5 cm mat, drying it in vacuum overnight, cutting it in half and curling the segment into a container made from 1 inch pipe. A piece of stainless steel screen lined the container so that the mat was exposed on both sides to the alkali. The pipe was then suspended in an oil bath at 123°C. After ageing, the mat was removed, unrolled, washed in hot water between screens until neutral, washed several times more, and then dried at 150°C and 432 mm of vacuum overnight. As samples became more brittle, it was difficult to remove the samples from the pipe container, thus mechanical losses began to be significant. Some samples made from heat-treated fibrids would not form good mats and disintegrated during ageing.

Results from these trials are shown in Table XXXI. Each mat made from heat-treated fibrids shows a higher weight loss than does the mat heat-treated under the same conditions. This was likely attributable to mechanical rather than chemical losses. The ageing of samples in water was done to give an idea of mechanical losses. Again, the mats made with heat-treated fibrids seemed to fare poorly. Although many other regimes of time and temperature for treatment could be explored, longer times at lower temperatures seemed to be more favorable since a more convenient, controllable, and reproducible process should result. One hour treatment at 375°C seemed to embrittle the sample sufficiently so that more stringent conditions might not be feasible.

In order to obtain better quality data, stainless steel containers were constructed into which four flat 2 inch diameter disks could be placed, interleaved with disks of stainless steel screen. These approximately half-gram samples were checked for weight loss after 25, 100, 250, 500 and 1000 hours. Besides an unheat-treated control sample, treatments of 1 and 4 hours at 250°C, and 1 hour at 375°C in the air oven were examined, both with loose fibrids and with formed mats. All of the heat-treated samples

TABLE XXXI. - WATER AND ALKALI AGEING OF PBI MATS

% Cumulative Weight Loss - Heat-Treated Mats

Treatment	none		1 hr @250°C		4 hr @250°C		1 hr @375°C	
Medium	H_2O[1]	KOH[2]	H_2O	KOH	H_2O	KOH	H_2O	KOH
Ageing time								
23 hr	(+1.4)	4.0	2.5	4.7	0	2.7	0	3.4,1.7
69.5 hr	(+0.9)	20.6	2.5	27.2			0.6	6.3,-
89.5 hr								- ,2.3

% Cumulative Weight Loss - Heat-Treated Fibrids Formed into Mats

Treatment	4 hr @250°C		1 hr @325°C		1 hr @350°C		1 hr @375°C	
Medium	H_2O	KOH	H_2O	KOH	H_2O	KOH	H_2O	KOH
Ageing time								
23 hr	2.1	6.3	1.3	9.8	(+0.2)	9.3	1.0	22.9[3],19.2[3]

(1) Immersed in water @50-60°C

(2) Immersed in 45% KOH at 123°C

(3) Sample disintegrated

were placed in vacuum at 155°C before ageing in KOH to assure the removal of adsorbed moisture and to permit a base weight to be determined.

After ageing the prescribed number of hours, the samples were removed and washed with successive changes of hot deionized water until a neutral pH was obtained. After an additional wash, the samples were dried under vacuum overnight at 155°C before weighing.

After the first 25 hour test period, it was observed that overnight drying (approximately 16 hours) in the vacuum oven at 155°C seemed insufficient to remove all traces of moisture from the samples. They were then placed in the vacuum oven for an additional 16 hours and reweighed. For the remainder of the tests, a minimum of 24 hours of drying at 155°C in vacuum was used with slight nitrogen bleed in the oven to assist in purging water from the system.

Although some samples may not have been rigorously dried and would therefore be expected to have a somewhat greater weight loss than indicated, only one sample, the mat treated for 1 hour at 375°C, had less weight loss than the control. Nevertheless, all weight losses exceeded the project target value of <1.5% after 5000 hrs.

All samples except the 375°C one and the control were discontinued at 250 hours because of sample disintegration. As expected, heat-treated fibrids produced mats that were brittle and did not retain their integrity beyond 100 hours. These data are summarized in Table XXXII.

The environmental ageing of both the control mat and the mat heat-treated in an air oven at 375°C for one hour was continued. Extension of this test to 502 hours resulted in the control gaining a bit of weight to give a cumulative loss of 2.8% while the 375°C treated sample lost weight to total 3.5%.

It was decided at this time to go back and recheck the original premise, that PBI drawn textile yarn would survive long term ageing in hot concentrated caustic with negligible weight loss. We were able to locate a retain of the sample of PBI crimped staple fiber which had been supplied several years ago to United Technologies for testing (24). This sample was carefully washed with water and isopropyl alcohol to remove any textile lubricant and was then dried

TABLE XXXII. - ALKALI AGEING OF PBI MATS

% Cumulative Weight Loss - Heat-Treated Mats

Treatment[1]	None	1 hr @ 250°C	4 hr @ 250°C	1 hr @ 375°C
Ageing time[2] (hrs)				
25	0.4%	(+0.2%)[3]	1.8%	(+0.2%)[3]
100	2.4%	1.7%	4.6%	1.7%
246	3.2%	4.7%	5.9%	2.7%
502	2.8%	(4)	(4)	3.5%

% Cumulative Weight Loss - Heat-Treated Fibrids Formed into Mats

Treatment[1]		1 hr @ 250°C	4 hr @ 250°C	1 hr @ 375°C
Ageing time[2] (hrs)				
25	-	1.2%	0.7%	11.3%
100	-	3.1%	2.4%	-
Sample Condition	-	(4)	(4)	(4)

(1) Heated in an air oven

(2) Hours of static immersion in 45% aqueous KOH @ 123°C (253°F)

(3) Apparent % weight gain

(4) Disintegrated

to constant weight in vacuo at 155°C. A 3.9 g sample exposed to 45% aqueous KOH for 21 hours lost 0.8% weight after being washed neutral and dried in vacuo to constant weight. The sample was then returned to fresh KOH bath for additional ageing.

We also located a fresh sample of PBI yarn that was drawn in 1978. This sample was not crimped or cut into staple as the earlier one had been but otherwise was treated in the same manner. As shown in Table XXXIII, both of these yarn samples showed excellent caustic resistance, losing only 2-2.5% weight after 1000 hrs. However these values still exceed the 1.5% contract target.

From the data available up to this point, it was concluded that a fibrid mat loses about twice as much weight as does drawn textile yarn. Oxidative heat treatment with this particular lot of fibrids did not increase the alkali resistence. Additionally, a mat heated in air at 150°C for 24 hours had a weight loss of 2.3% after 24 hour treatment in alkali. In order to increase the severity of oxidation over the previously tested 375°C, mat samples were treated to 400, 450, and 500°C temperatures for an hour. Severe shrinkage, weight loss, and darkening were noted as shown below:

Treatment:	1 hr. @ 400°C	1 hr. @ 450°C	1 hr. @ 500°C
Color	Dark	Brown	Black
Shrinkage	7%	13%	69%
Weight Loss	12%	19%	95%

Each mat was subsequently aged in aqueous KOH for 24 hours. The sample which was heat treated at 400°C seemed to gain weight (+3.8%); however, this may be the result of an inadequate washing-drying cycle. The 450°C treated sample sustained a 6.3% weight loss. Both of these mats were too brittle to be handled or tested further. The third sample, treated at 500°C, disintegrated to an extent that no ageing information could be gained. It would seem that even under conditions which lead to extensive oxidation, the mat samples remain subject to attack by hot concentrated alkali.

TABLE XXXIII. - ALKALINE AGEING OF DRAWN TEXTILE YARN

Time (hr)[1]	Cumulative Weight Loss (%) 70's Sample	1978 Sample
21	0.8	0.7
99	1.1	1.0
243	1.3	1.3
500	1.7	1.7
1000	2.5	2.1

[1] Hours of static immersion in 45% aqueous KOH @ 123°C (253°F).

All of the mats tested were made with the same lot of fibrids (26374-19) used by Kimberly-Clark for fabrication of a large quantity of alkaline battery mats. These fibrids were prepared from a particular PBI polymer which was produced early in 1978. For purposes of comparison, mats were made for testing from two earlier alkaline battery fibrid samples. The earlier one (26084-3) was prepared from dope recovered from the PBI spinning pilot plant. This dope had been in the equipment piping for several years. All PBI fibrids prepared prior to November 1977 were made from this particular polymer dope. In order to scale up fibrid production to conduct trials at Kimberly-Clark, two batches of PBI yarn were solutioned in November 1977, since this was the only source of PBI available at the time. Fibrid 26084-34 was made from this dope, as was the material used by Kimberly-Clark for the continuous paper trial in January 1978. Ageing of mats from these various PBI sources under the usual conditions (45% KOH @ 123°C) produced the weight loss data shown below:

Sample Number	Polymer Source	Cumulative Weight Loss (%) 24 hr.	100 hr.	250 hr.	500 hr.
26374-19	1978	0.4	2.4	3.2	2.8
26084-34	yarn	4.1	5.5	7.0	-
26084-3	dope	3.7	4.4	4.9	-

From this data, it appears that there are real differences between samples and that fibrids prepared from the more recent, new polymer are more resistant to hot alkaline solutions than are the fibrids made from the older polymers. On the other hand, the weight loss resistance shown by the samples of drawn textile yarns remains significantly superior to any of the fibrids.

In addition to the improved weight loss resistance of the 1978 polymer, it was also observed that the shrinkage during ageing was less, as was the degree of embrittlement and cracking. From these observations, it may be reasonable to conclude that there are variations in the basic chemical structure of PBI which contribute, at least in part, to the differences being experienced in resistance to alkali attack.

It was discovered that heat treatment at 250°C, even for four hours, was insufficient to crosslink a PBI mat enough to render it insoluble in hot dimethylacetamide. However, at 375°C, the sample so treated was no longer soluble in hot dimethylacetamide. This is indicative of the presence of crosslinking.

The -19 fibrids, which turned out to be the best, were used for all of the studies on thermo-oxidative stabilization. Since alkaline weight loss for the control sample could have reached its maximum, after 500 hours of testing, the mat was returned to the test cell to extend the test period to 1000 hours to verify this idea. However, since the mat was in poor shape, it was decided to test a second mat made from -19 fibrids in addition to the original one.

To minimize handling, the new sample was not removed from the test cell for weighing prior to 250 hours. Since the best thermally oxidized sample was the one heated for one hour at 375°C, ageing of that one was continued as well. A new sample, heat-treated for one hour at 375°C was made to compare with the -19 control. A sample of this heat-treated mat was tested for its solubility at room temperature in dimethylacetamide prior to ageing to prove it sufficiently oxidized and cross linked to be insoluble. Since larger test cells were available by then, single nominal 9 cm diameter samples were used rather than the multiple 5 cm ones used previously.

The data in Table XXXIV show the cumulative weight loss for both the old sample (small diameter) reported earlier and the new larger diameter mats. In both cases, the mat which was heat-treated for one hour at 375°C in an air oven was found to have significantly less weight loss than the control. It also seemed to have better integrity. When the old samples were placed back in the bath to resume testing at 500 hours, they were both brittle and disintegrating. By 1000 hours, the control had crumbled. On the other hand, the heat-treated sample was in a better condition with some pieces of the original disk left. Thus, the high weight loss seen for the control at 1000 hours (10.3%) may include high mechanical losses.

For the new samples, diameter as well as weight loss was measured in order to determine shrinkage. However, some shrinkage may be due to the drying cycle necessary each time the sample is weighed. The initial drying prior to alkaline ageing resulted in a 3.2% shrinkage in diameter for the control sample and a 2.1% shrinkage for the heat-

TABLE XXXIV. - WEIGHT LOSS OF PBI MATS IN ALKALI

Exposure (hr)	% Cumulative Weight Loss[1]			
	Control		Heat-Treated[2]	
	Old	New	Old	New
24	-0.4	-	(+0.2)	-
100	-2.4	-	-1.7	-
250	-3.2	-2.7	-2.7	-1.7
500	-2.8	-2.1	-3.5	-1.2
750	-6.2	-5.5	-3.8	-1.9
1000	-10.3	-9.9	-4.8	-1.9

[1] In 45% KOH at 123°C

[2] Heat-treated 1 hour @375°C.

treated one. By 260 hours, the control was cracked in several places and cracked while being bent around the radius of an ordinary pencil. As shown in Table XXXV, the diameter shrinkage was 19.8%, i.e., the diameter went from 9.1 to 7.3 cm. On the other hand, the heat-treated sample had only a few edge cracks and could be bent over a pencil. Shrinkage was only 10.6% (9.4 to 8.4 cm) and weight loss was low (1.7%). At 500 hours, the control mat broke in half while the heat-treated one could still pass the pencil test. By 760 hours, the control was broken into several pieces, thus exhibiting brittleness, while the heat-treated sample remained flexible. By the end of the test period, the control mat was largely disintegrated while the heat-treated one after drying was substantially intact, although brittle and easily cracked by handling.

Upon removal from the test cell, the heat-treated mat was found to have the same diameter as when it was put in 250 hours earlier. Upon washing and drying, it shrunk from 6.5 to 5 cm in diameter (23%). This suggests that mat shrinkage occurs during the drying step rather than in the test cell so that under actual use conditions, little to no shrinkage should be noted.

I. Preparation of Mats by Preferred Procedure

1. Fibrids

Prepare a 15-24% by weight PBI dope in dimethylacetamide (DMAc) containing 2% lithium chloride based on weight of DMAc. Dissolve by heating for 2 hours at a temperature of 200-220°C. After cooling below the boiling point of DMAc (165°C), filter the dope to remove insolubles. Dilute the dope with DMAc until it has a viscosity of 5 poise (Brookfield RTV, Spindle #2 at 10 rpm, 25°C). This will occur at a solids level of about 10.5%. Filter again before using with cloth or felt to remove any trash picked up during dilution.

The fibrids spray apparatus is set up to feed room temperature deionized water to the air side of a Spraying Systems 1/4J pneumatic atomizing nozzle assembly with the PBI dope fed to the fluid side. Fluid nozzle 2050 with air cap 73160 was used. Dope is fed to the nozzle at a rate of 48.5 g/min. Coagulant pressure should be 1.03 MPa (150 psi) giving a flow rate of 2.9-3.0 kg (6.4-6.6 lb) per minute.

TABLE XXXV. - SHRINKAGE OF PBI MATS

Exposure	Cumulative Shrinkage (%)	
	New Control	New Heat-Treated[1]
260	19.8	10.6
500	25.3	20.2
760	Broken	30.8

Note: On initial drying at 155°C in vacuo prior to exposure, the control shrunk 3.2% while the heat-treated sample shrunk 2.1%.

[1] Heat-treated 1 hour @375°C.

The resulting fibrids are separated from the mother liquor and are boiled in four changes of deionized water. They are then suspended in toluene and the water removed by distillation of the toluene-water azeotrope. When water no longer comes off, the fibrids are filtered from the toluene and are dried in a vacuum oven at 80°C.

2. Mats

Weigh out the calculated amount of dry fibrids, according to the desired basis weight of the mat, and soak in deionized water for a minimum of one hour. Break up any lumps by hand. Disperse the slurry with a Waring blender and form the mat by filtration in a suitably sized hand sheet box. Remove the damp mat from the box, overlay it with a sheet of filter paper or a blotter and lightly roll by hand to transfer the wet mat to the overlay. Remove the mat from the initial forming screen or paper, place dry paper or blotters on the mat, and calender the mat if desired. Dry under weights, either at ambient for several days or on a hot plate.

3. Heat Treatment

Heat treat the mat by placing in a static air oven at 375°C for one hour. Monitor the solubility of a portion of the heat treated mat in DMAc at room temperature until it is no longer soluble.

CONCLUSIONS

PBI polymer can be readily converted into fibrids by use of a commercial pneumatic atomizing nozzle. Water is the preferred coagulant. Mats with good handling strength are obtained by filtering an aqueous slurry of PBI fibrids, but excessive shrinkage, presumably due to the high moisture affinity of PBI, tend to produce excessive wrinkles upon drying. A process to overcome this was developed, consisting of washing out the residual DMAc solvent and then distilling the water from the fibrid while being slurried in toluene in order to pre-shrink the fibrids. In this manner, dry fibrids were prepared which were rewettable and could be redispersed in a blender to prepare mats with low shrinkage.

Mats with varying combinations of basis weight, thickness, and permeability were made from the same basic lot of fibrids. Calendering, either wet or dry, seemed particularly effective in adjusting the mat parameters to fit target values. Originally, two different fibrids were made, varying in coarseness for the two uses, battery and fuel cell separators. Later, it was demonstrated that it is possible to prepare fuel cell mats from the coarser battery fibrids by a more severe calendering operation.

Scale-up of the fibrid process was achieved in a pilot plant. A basket centrifuge was used for separations and a 1400 l (400 gal.) stainless steel reactor was used for washing. The preshrinking operation was accomplished by azeotropically distilling water from the fibrids in a toluene slurry.

Scale-up to a continuous paper machine was tried by the Schwitzer Division of Kimberly-Clark Corporation. Assessment of handsheets led them to adding 20% of an ultrafine PBI fibrid slurry in DMAc-water to increase web strength and handleability. Upon trial on the paper machine, wet fusion resulted from incomplete removal of the DMAc solvent prior to drying. Rather than continue trials to prepare a continuous web, Kimberly-Clark agreed to prepare sufficient 30x60 cm (12x24 in.) handsheets to allow evaluation by NASA. These handsheets, as ultimately delivered, contained 30% of the ultrafine fibrid to improve handling strength.

While the alkaline stability of PBI is excellent, some samples of fibrid mats seemed to be chemically attacked. Since textile yarn is drawn at high temperature during processing, with accompanying oxidation of the structure such as to render it insoluble, suitable oxidative heat treatments were sought for PBI fibrids in order to improve their stability. Heat treatment of fibrids produced a somewhat darkened and shrunken material which could no longer be fabricated into a mat with any integrity. On the other hand, similar heat treatment of a formed mat, such that the mat is no longer soluble in DMAc, gave a material which had improved stability to hot concentrated alkali, similar to that found for textile fiber.

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